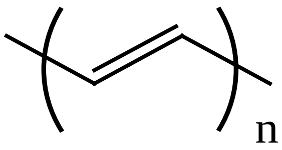
UNIVERSITÉ LAVAL

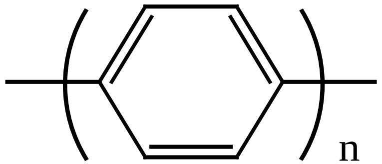
NEW POLYMERIZATION METHODS FOR PLASTIC ELECTRONICS

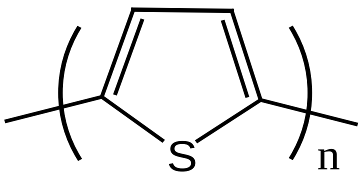
Mario Leclerc…

and many others

CONJUGATED POLYMERS







- **ELECTRICAL PROPERTIES**

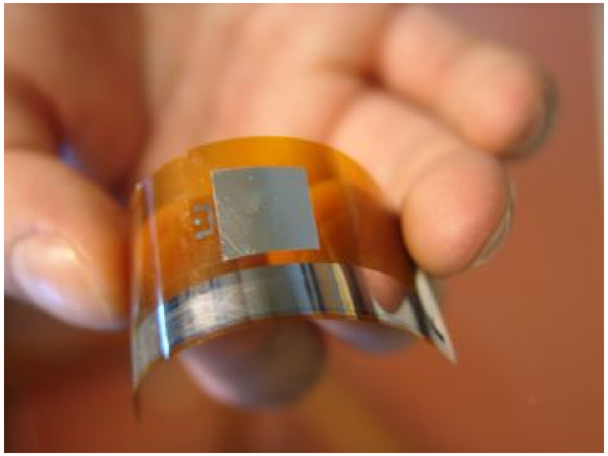
Semiconductors to conductors

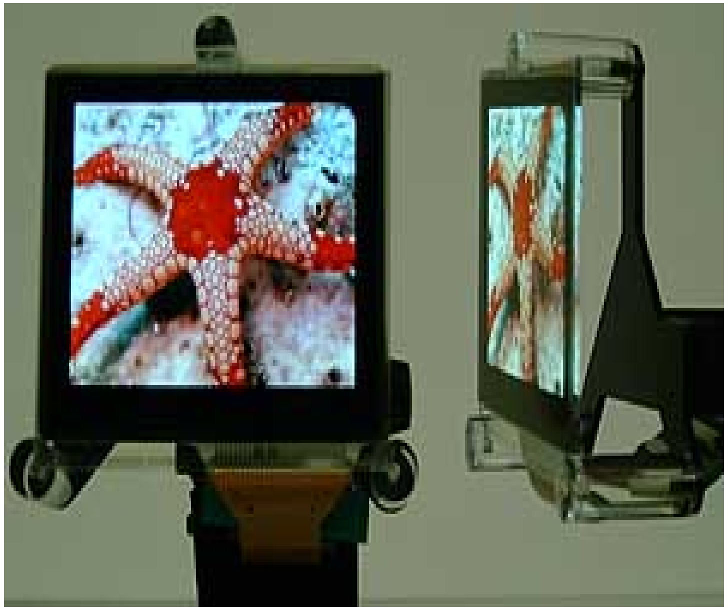
- **OPTICAL PROPERTIES**

Absorption and emission in the UV-visible range

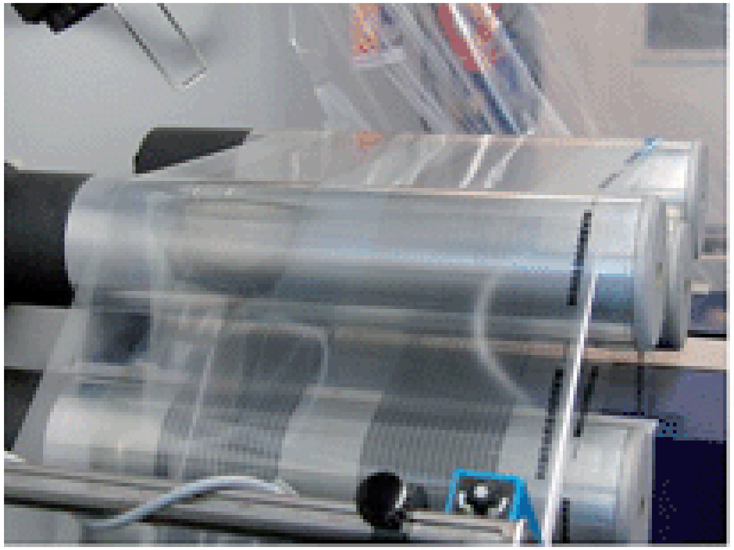
- **STABILITY, MECHANICAL PROPERTIES**

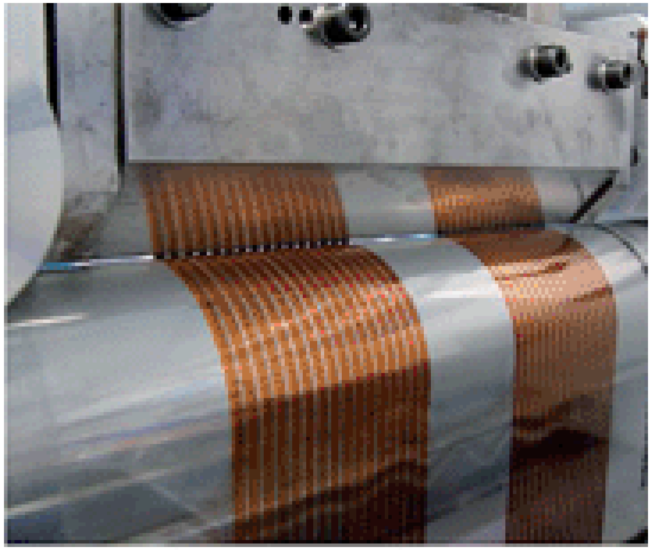
PLASTIC ELECTRONICS

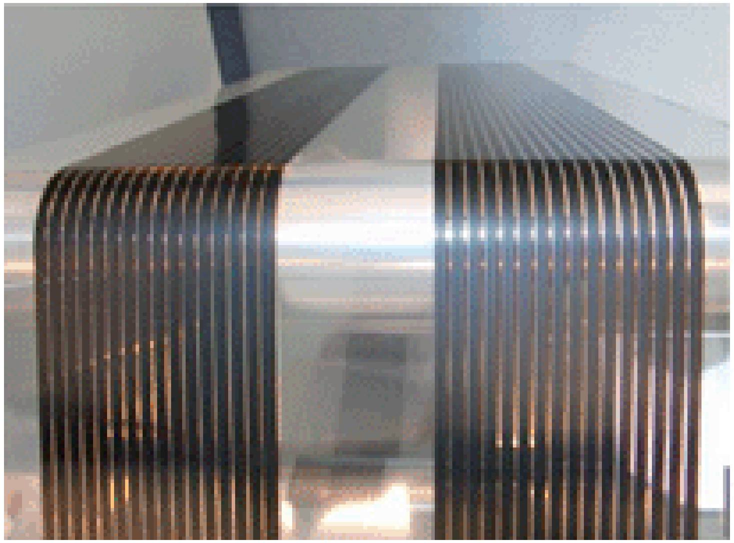


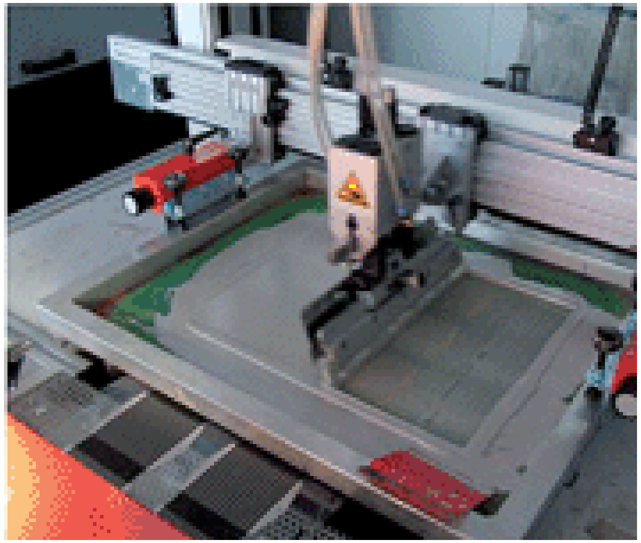


10-10-10 challenge

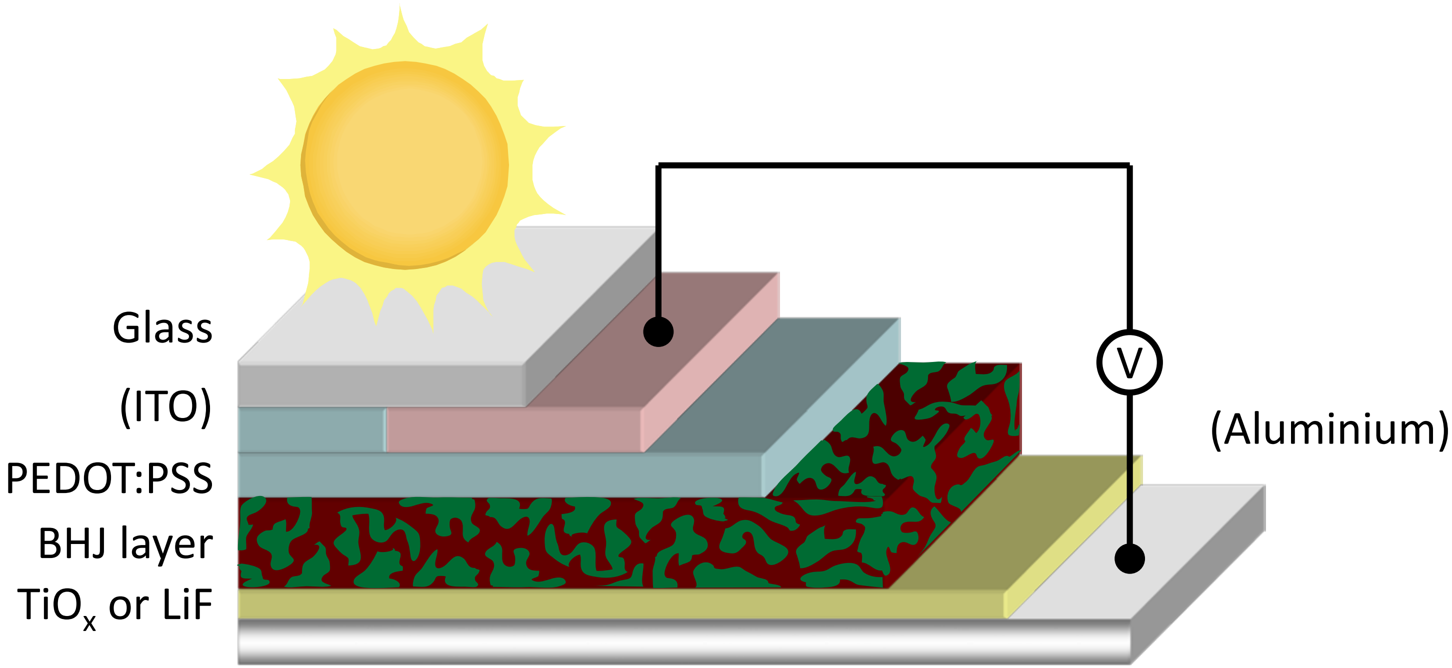






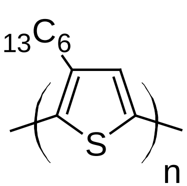


BHJ Solar Cells



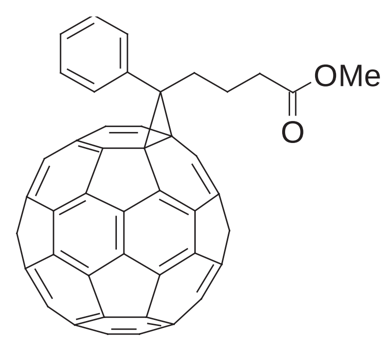
BHJ layer

Polymer



P3HT

Fullerene

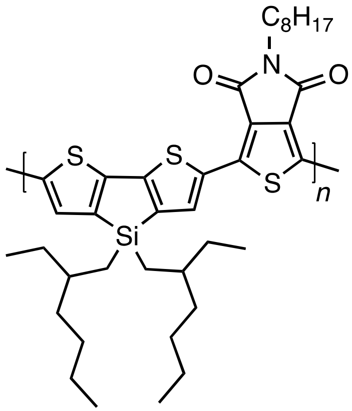


PCBM-C$_{61}$

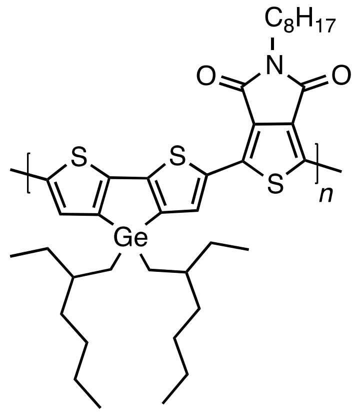
Industrial materials

Group	PCE	System
Heliatek	12%	Small molecules, tandem
Konarka	9 %	Polymers
UCLA/Solarmer	10.4 %	Polymers, tandem
Polyera	9.2%	Polymers?
Mitsubishi	10-11%	Small molecules

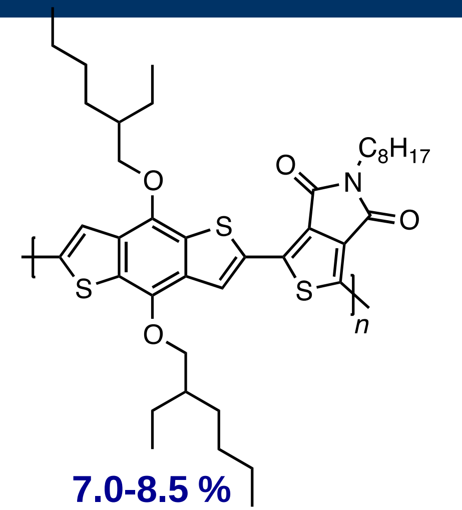
Some Landmark Materials for OPV



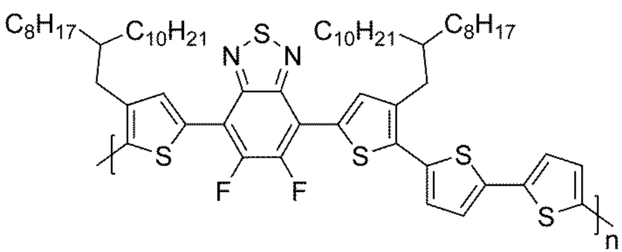
8 %
Lu, Leclerc, Tao



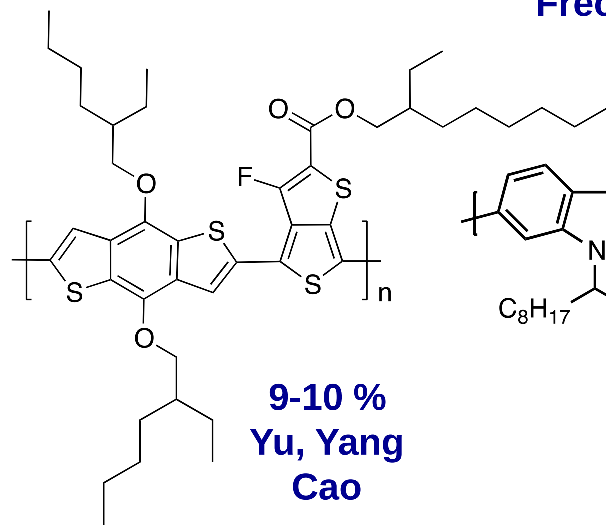
8.5 %
Reynolds, So



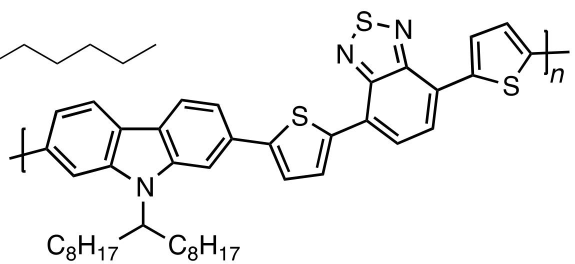
7.0-8.5 %
Leclerc, Tao
Fréchet, McGehee



10 -11 %
Ade, Yan

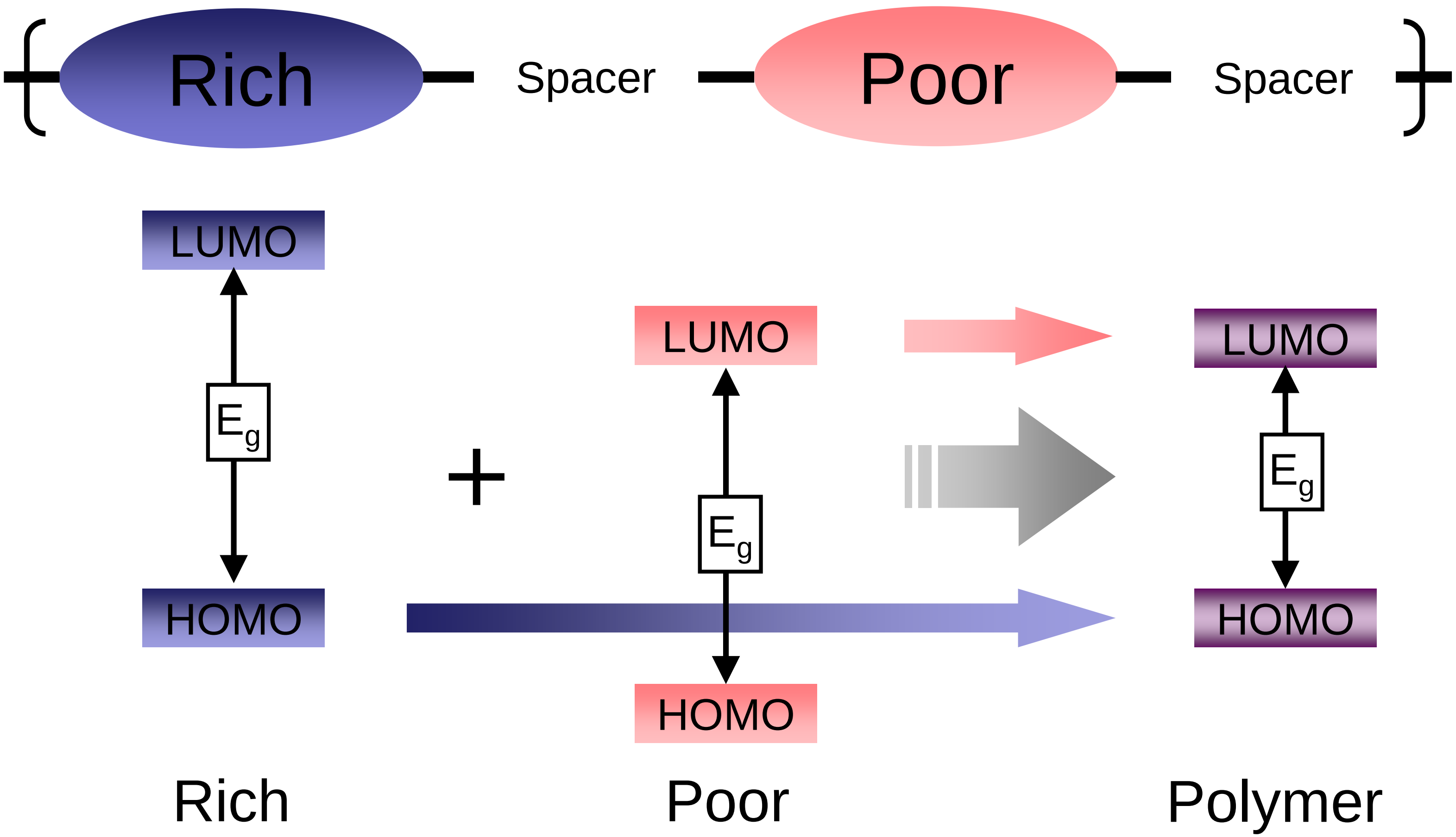


9-10 %
Yu, Yang
Cao



7-8 %
Leclerc, Heeger
Leclerc, Tao

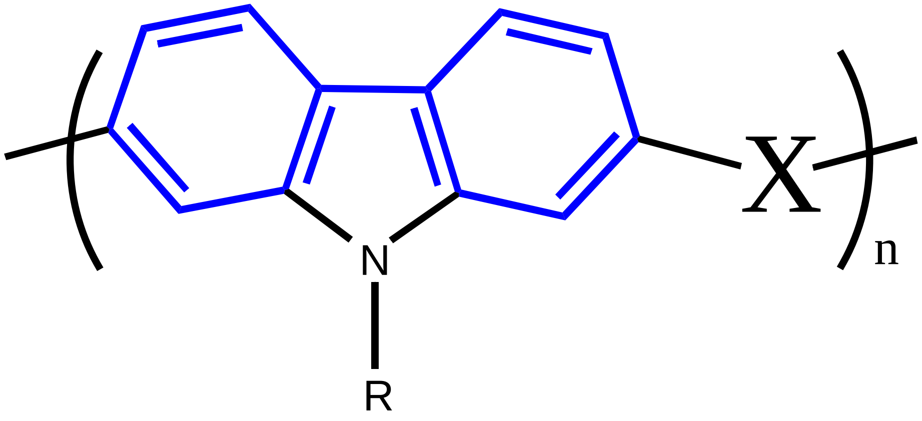
Low-Band-Gap Polymers



Mullekom, H. A. M. et al. *Mater. Sci. Eng., R.* **2001**, *32*, 1.
Roncali, J. *Macromol. Rapid Commun.* **2007**, *28*, 1761.

Polycarbazoles

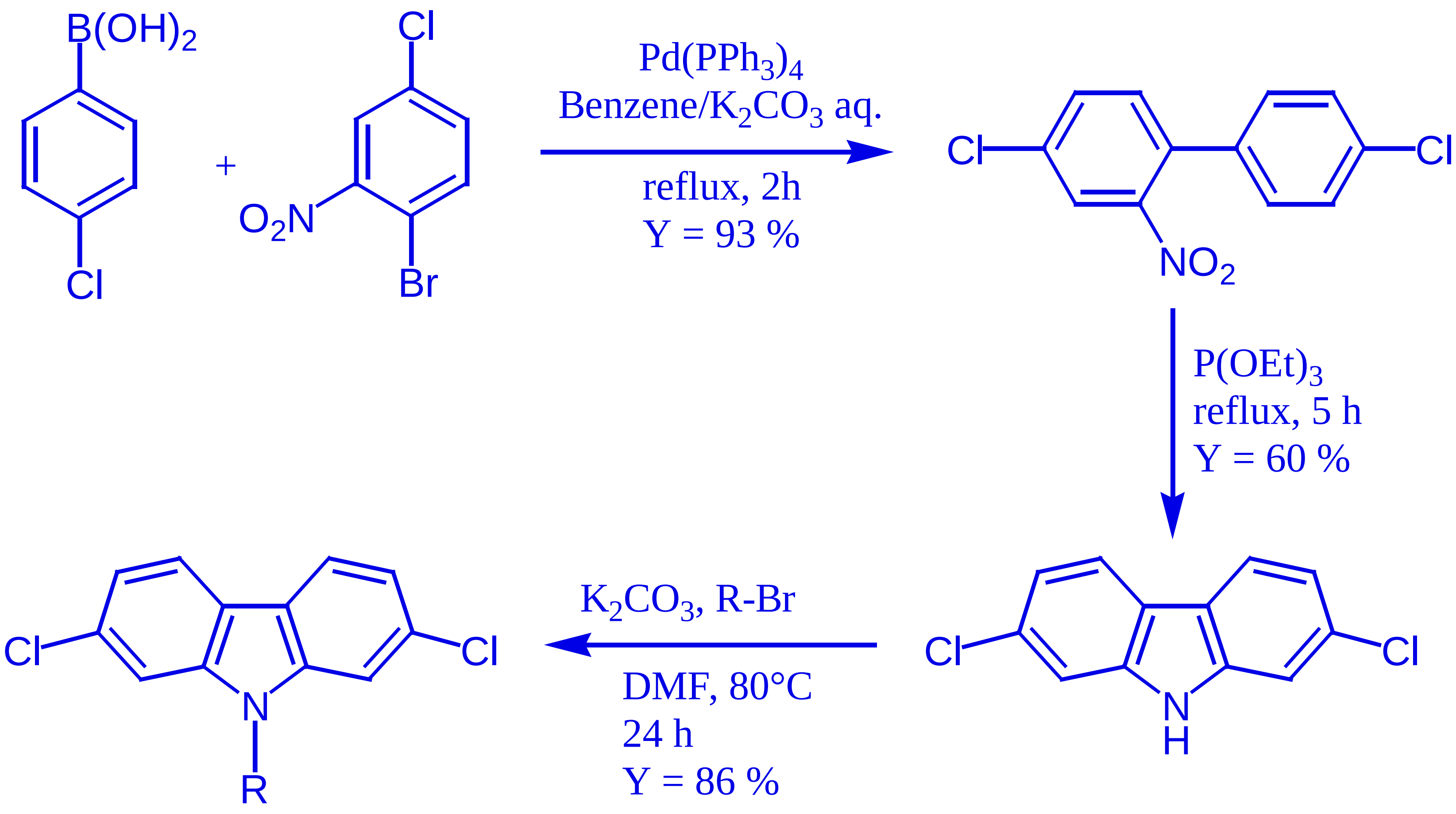
Our Approach



Poly(*N*-alkyl-2,7-carbazole)s

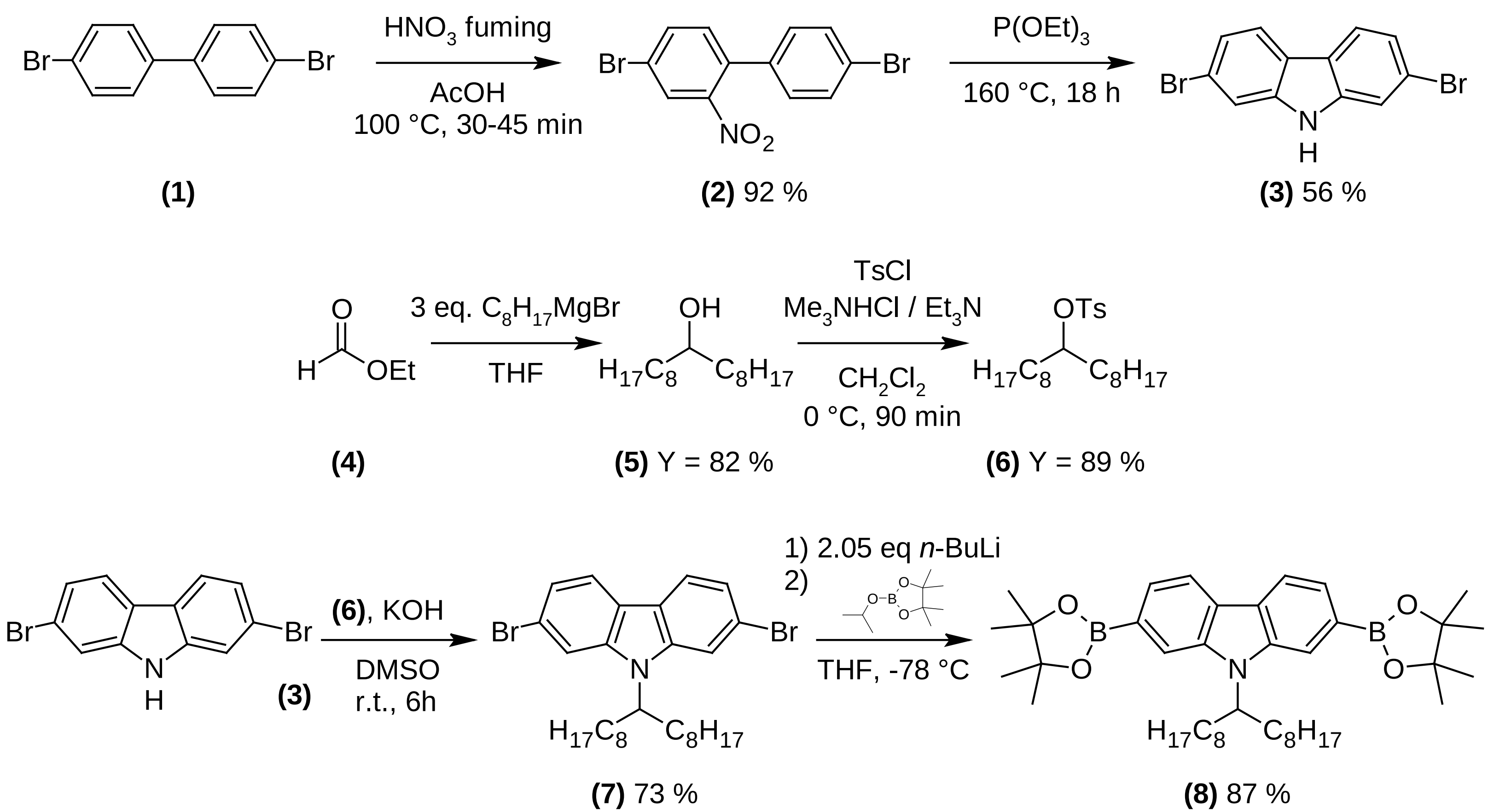
⇒ Fully aromatic
⇒ Good hole transport
⇒ Easy substitution on nitrogen atom

Polycarbazoles



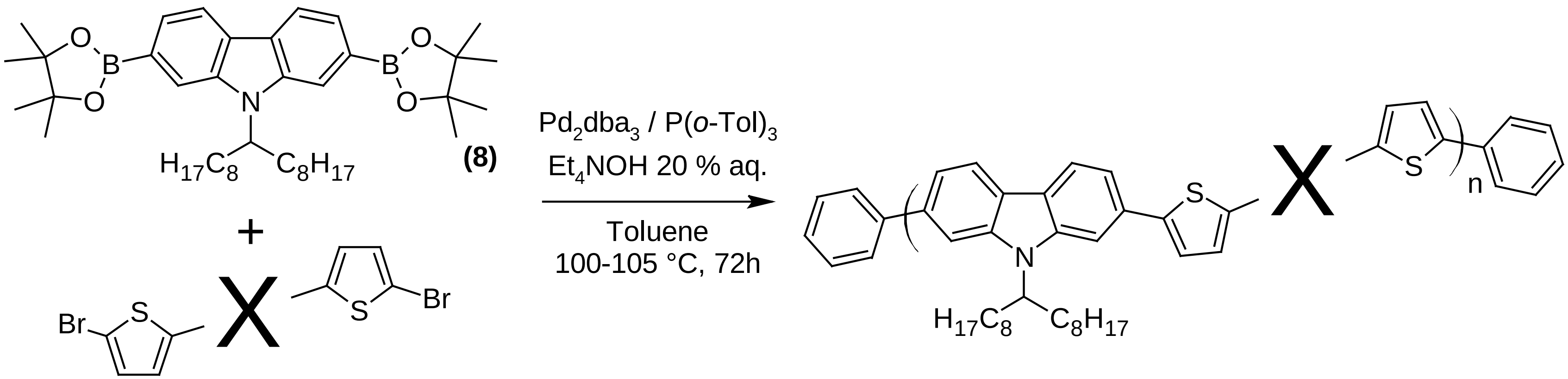
Morin, J.-F.; Leclerc, M. *Macromolecules* **2001**, *34*, 4680.

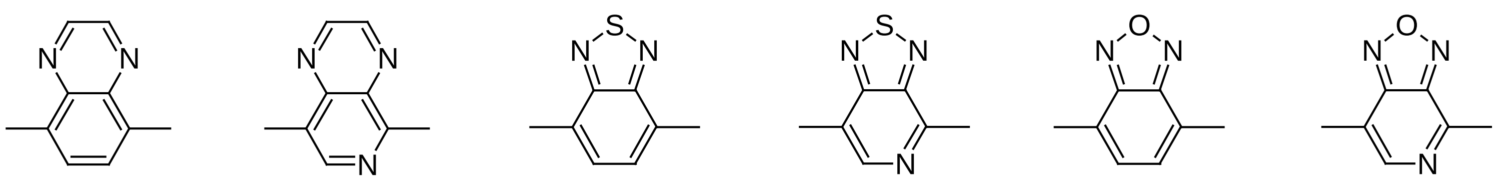
Synthesis – Carbazole Monomers



Dierschke, F.; Grimsdale, A. C.; Müllen, K. *Synthesis* **2003**, 2470.
Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater*., **2007** 19, 2295.

Low-Band-Gap Poly(2,7-carbazole)s





PCDTQx	PCDTPP	PCDTBT	PCDTPT	PCDTBX	PCDTPX
M_n = 9 KDa	M_n = 11 KDa	M_n = 36 KDa	M_n = 4 KDa	M_n = 26 KDa	M_n = 5 KDa
M_w = 14 KDa	M_w = 19 KDa	M_w = 55 KDa	M_w = 6 KDa	M_w = 52 KDa	M_w = 6 KDa

Non-optimized polymerisation conditions for some polymers

Poly(2,7-carbazole)s

Co-Monomers

Polymers

410 nm
(3.0 eV)

1100 nm
(1.1 eV)

Polym. Chem. 1, 127-136 (2010)

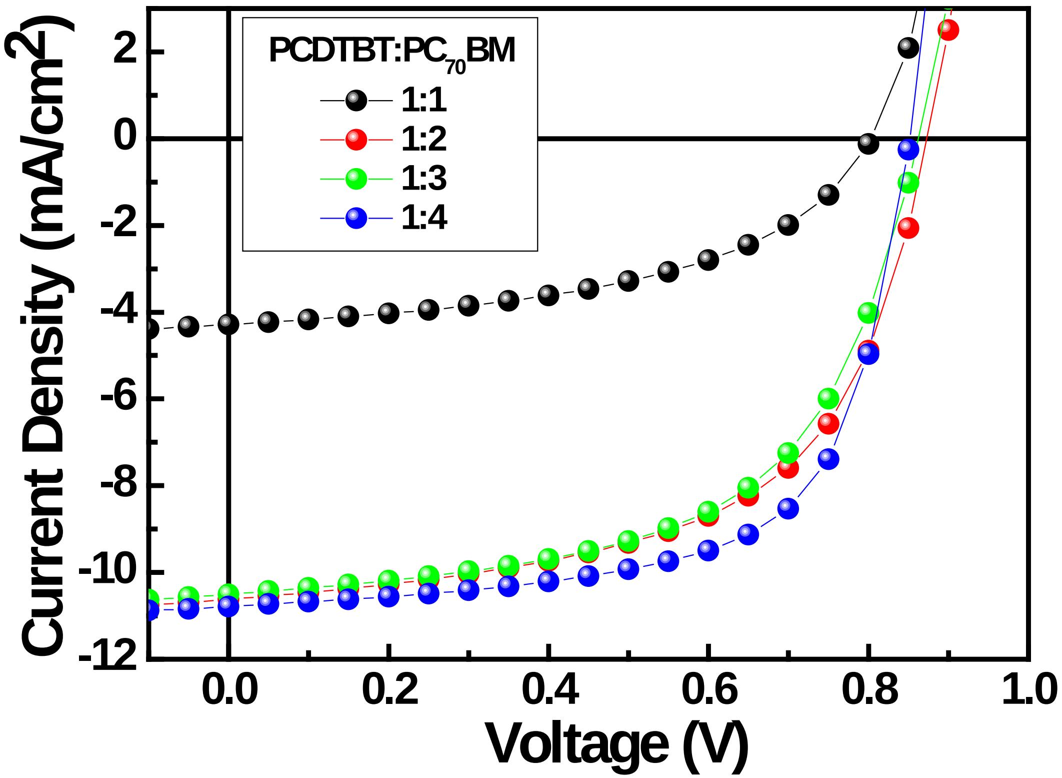
SOLAR CELLS

Heeger, Leclerc

Nature Photonics, 3, 297 (2009)

	J_{sc} (mA/cm²)	V_{oc} (V)	FF	E_{ff}(%)
1:1	4.3	0.8	0.5	1.7
1:2	10.6	0.87	0.58	5.34
1:3	10.5	0.86	0.58	5.23
1:4	10.8	0.85	0.65	6.0

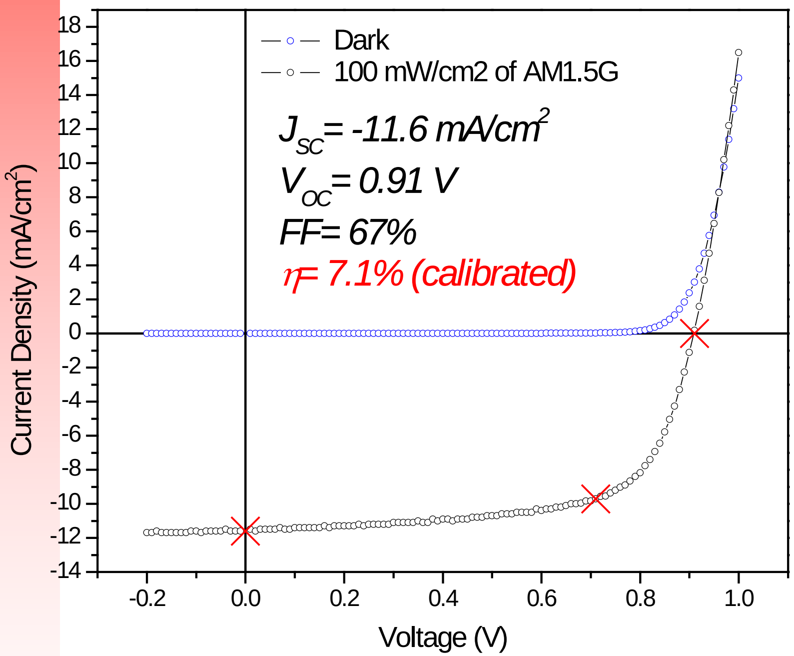
ITO/PEDOT:PSS/PCDTBT:PC_{70}BM/TiO_x/Al

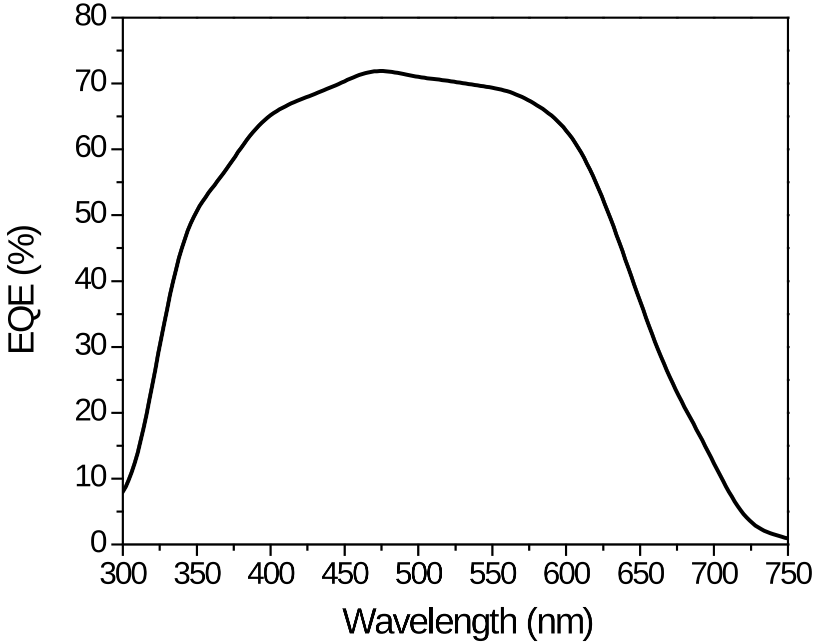


Recent results: PCDTBT

V_{oc}=0.913V, FF=66%, J_{sc} (EQE)=11.83mA/cm^2

PCE=7.1% (Single unit cell with 1 cm^2 active area)



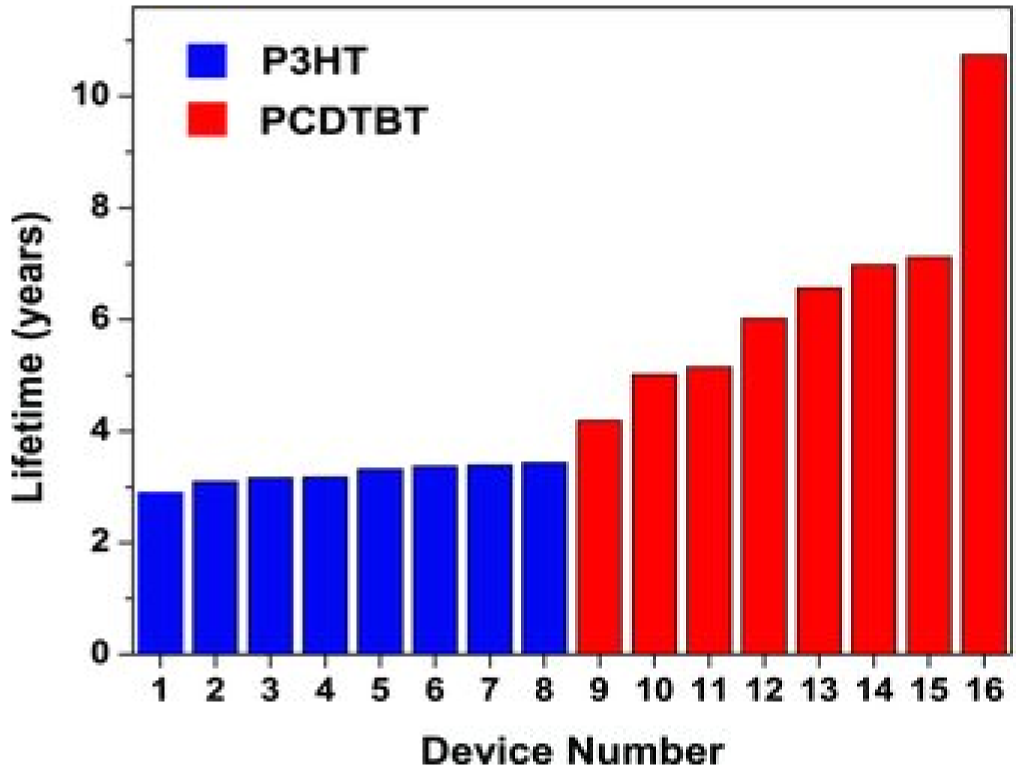


Y. Tao, IMS, CNRC, Appl. Phys. Lett., 98, 253301 (2011)

See also A.J. Heeger, PCE of 7.9%, *Adv Mater* **2013**, *25*, 7038

High Efficiency Polymer Solar Cells with Long Operating Lifetimes

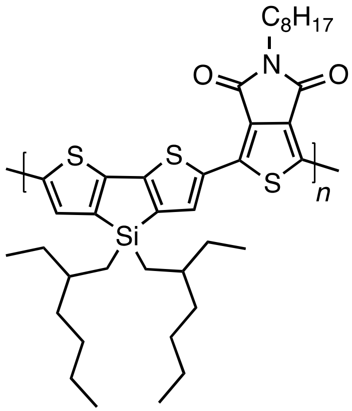
McGehee, Stanford



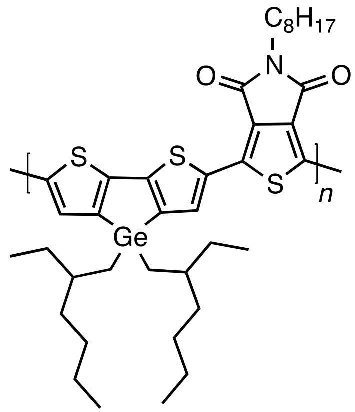
Advanced Energy Materials
Volume 1, Issue 4, pages 491-494, 20 APR 2011
See also: Nature Communications, 5:5688 (2014). Lifetime about 10 years

PCDTBT now available at SJPC

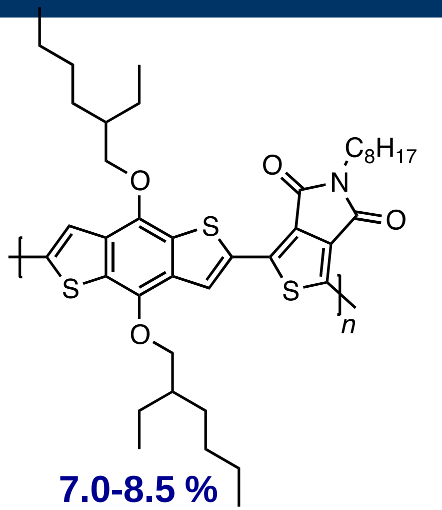
Some Landmark Materials for OPV



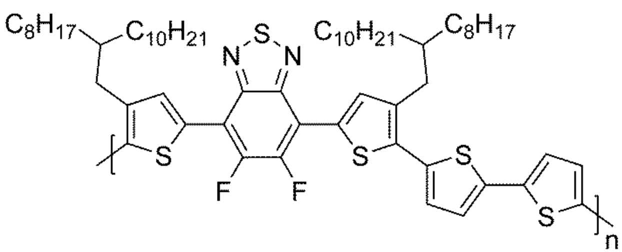
8 %
Lu, Leclerc, Tao



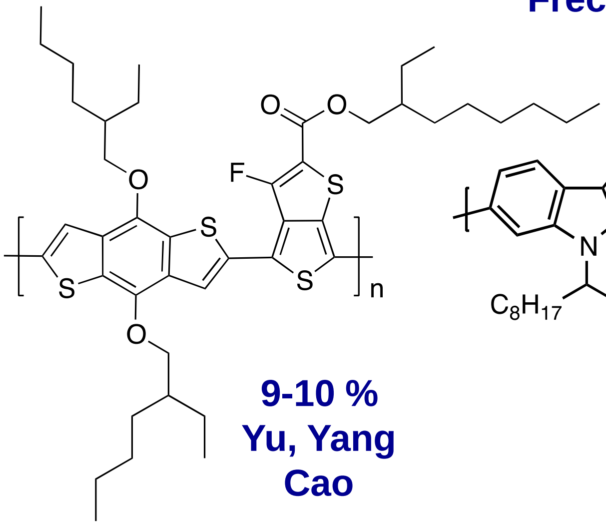
8.5 %
Reynolds, So



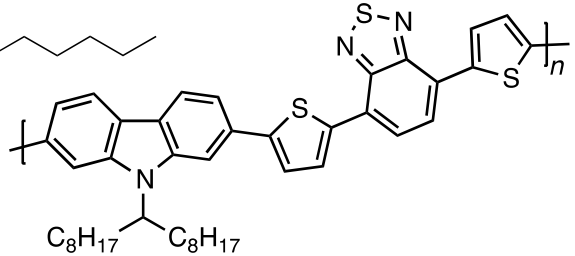
7.0-8.5 %
Leclerc, Tao
Fréchet, McGehee



10 -11 %
Ade, Yan

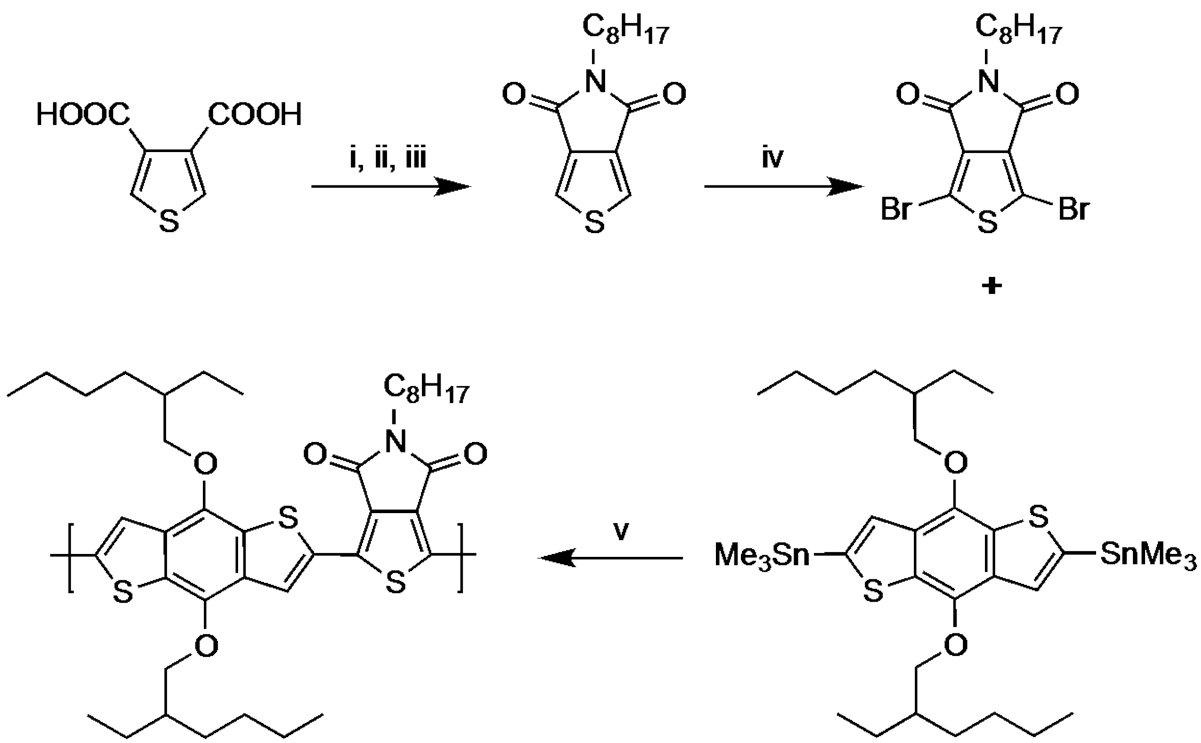


9-10 %
Yu, Yang
Cao



7-8 %
Leclerc, Heeger
Leclerc, Tao

First Synthesis of PBDTTPD



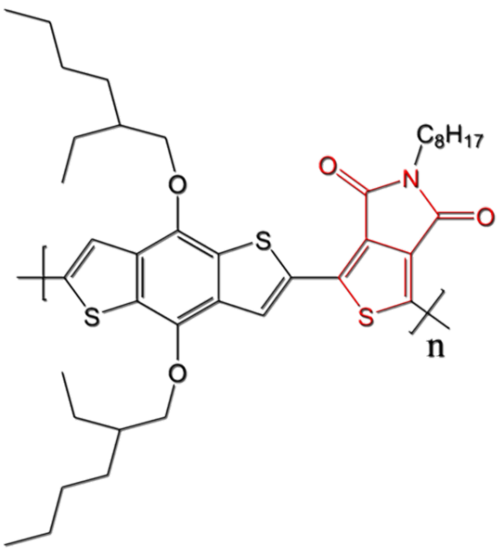
TPD

BDT

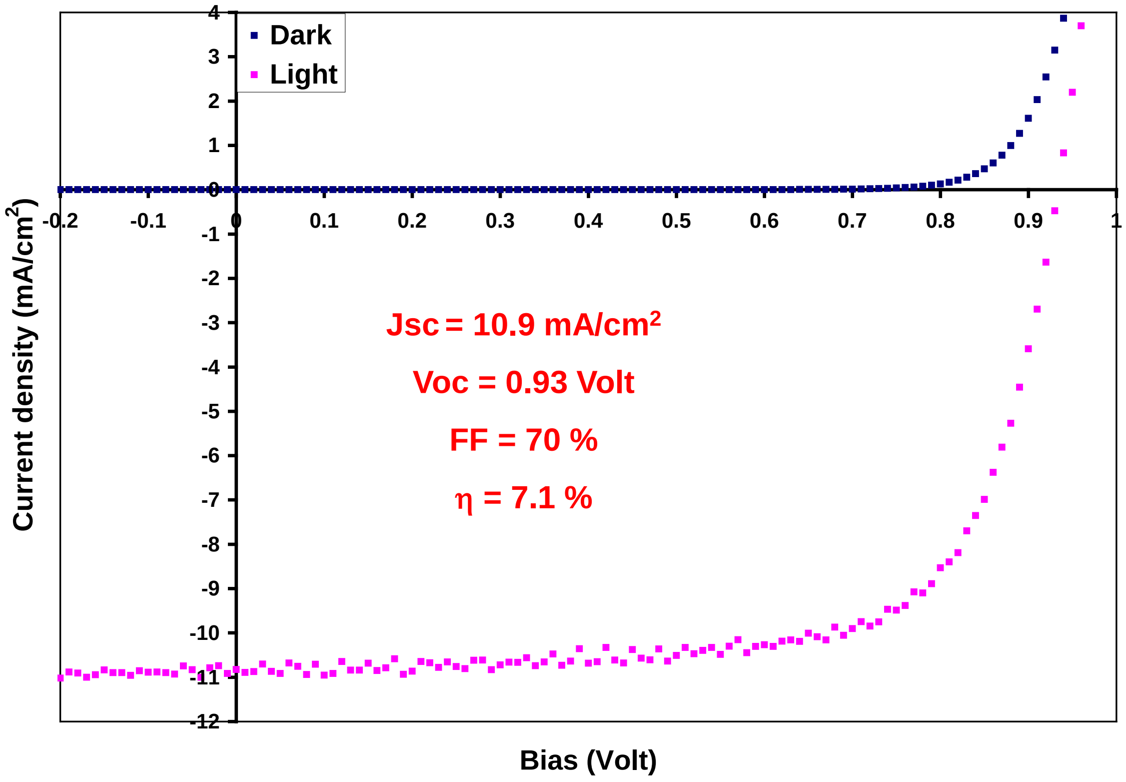
Conditions: i) Ac_2O, 140 ^oC, overnight; ii) n-$C_8H_{17}NH_2$, toluene, reflux 24 h; iii) $SOCl_2$, reflux, 12 h;   iv) H_2SO_4, CF_3COOH, NBS, rt, overnight; v) $Pd_2(dba)_3$, P(o-tolyl)$_3$, toluene, 110 ^oC, 48 h.

J. Am. Chem. Soc., 132, 5330 (2010)

Most recent results: PBDTTPD mixed with PC61BM



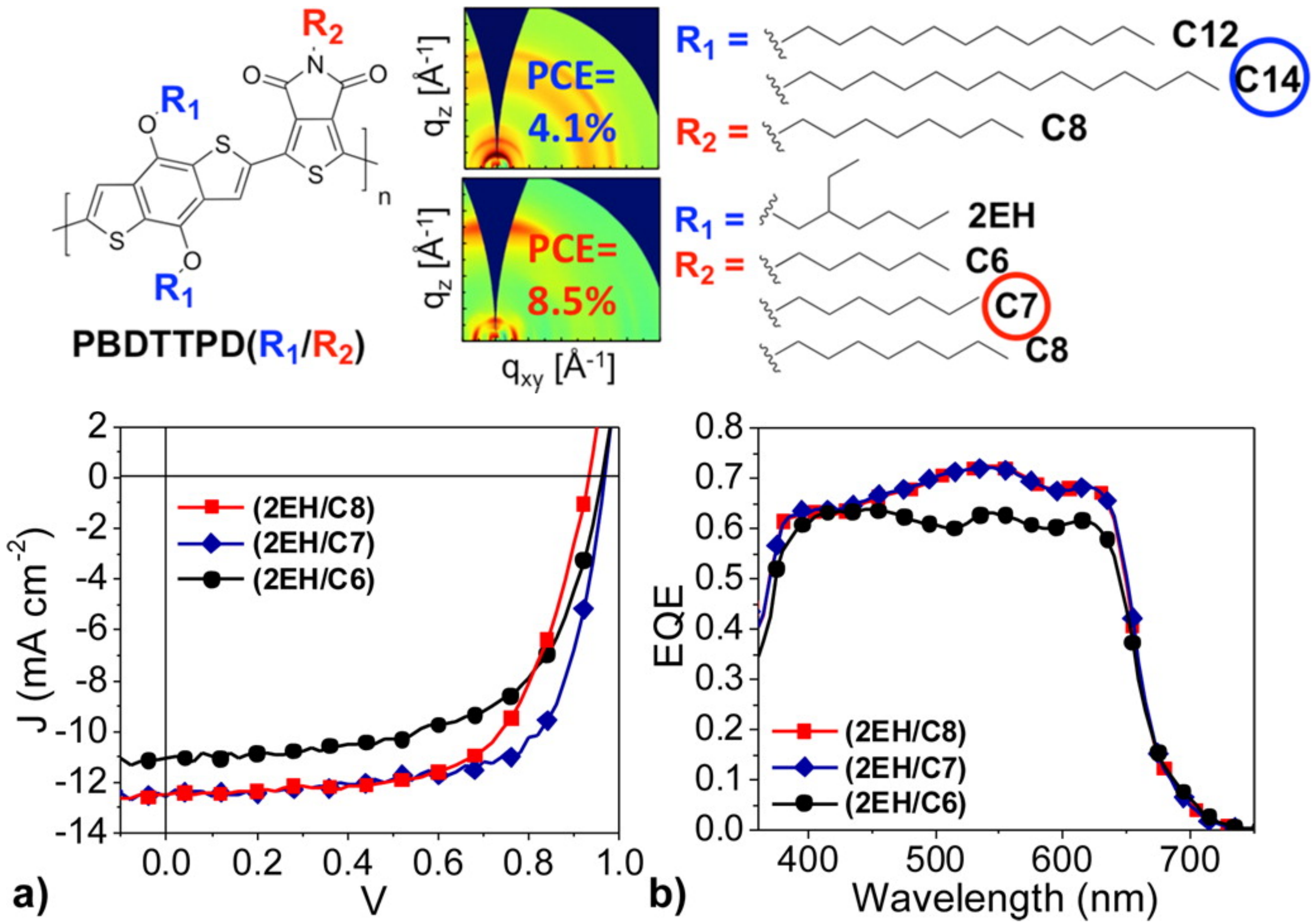
Surface: 1.00 cm^2



Y. Tao, IMS, CNRC, Ottawa

B. R. Aïch, J. Lu, S. Beaupré, M. Leclerc, Y. Tao, *Org. Electron.*, **2012**, 13, 1736

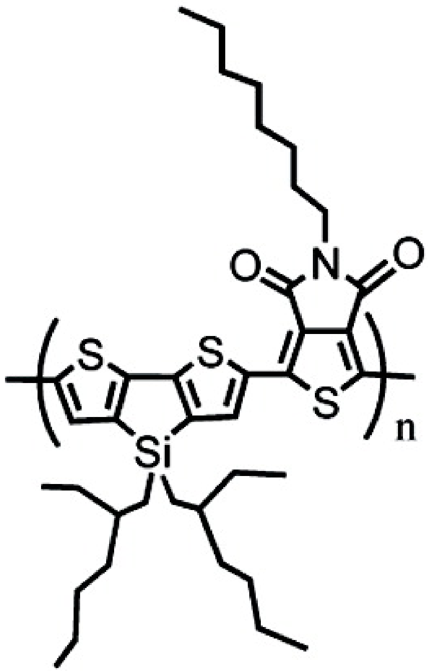
PCE of 8.5%



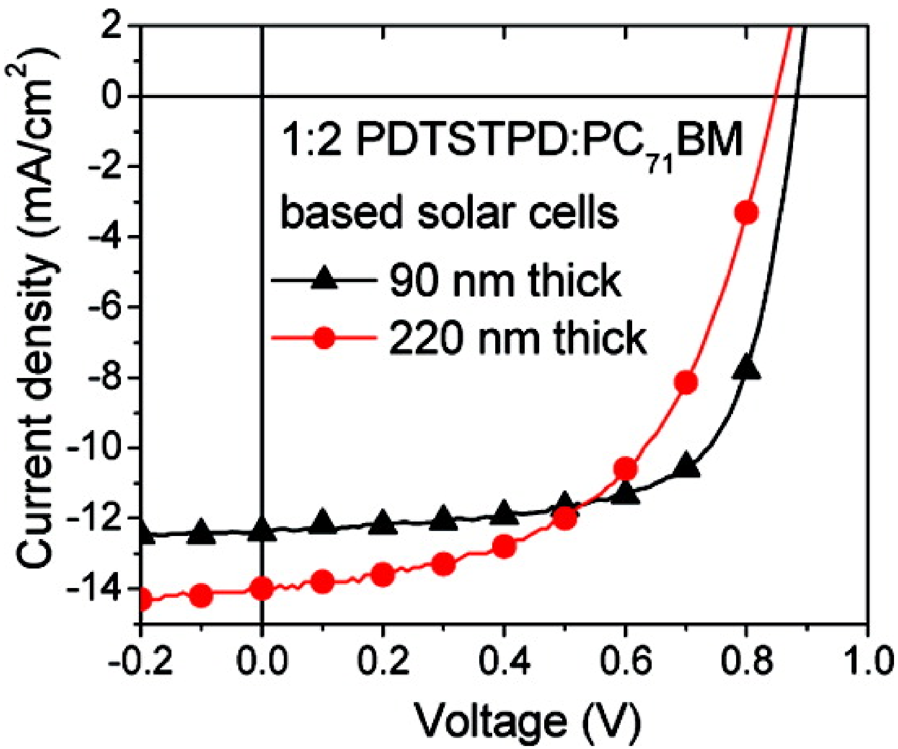
Published in: Clément Cabanetos; Abdulrahman El Labban; Jonathan A. Bartelt; Jessica D. Douglas; William R. Mateker; Jean M. J. Fréchet; Michael D. McGehee; Pierre M. Beaujuge; *J. Am. Chem. Soc.* **2013,** 135, 4656-4659.
DOI: 10.1021/ja400365b

New TPD-based copolymers

Efficiency of 7.3%

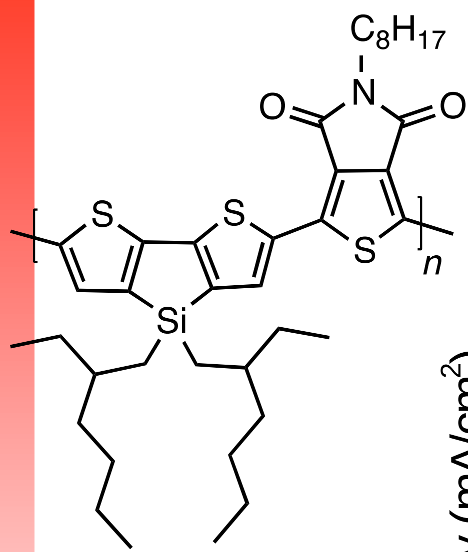


PDTSTPD

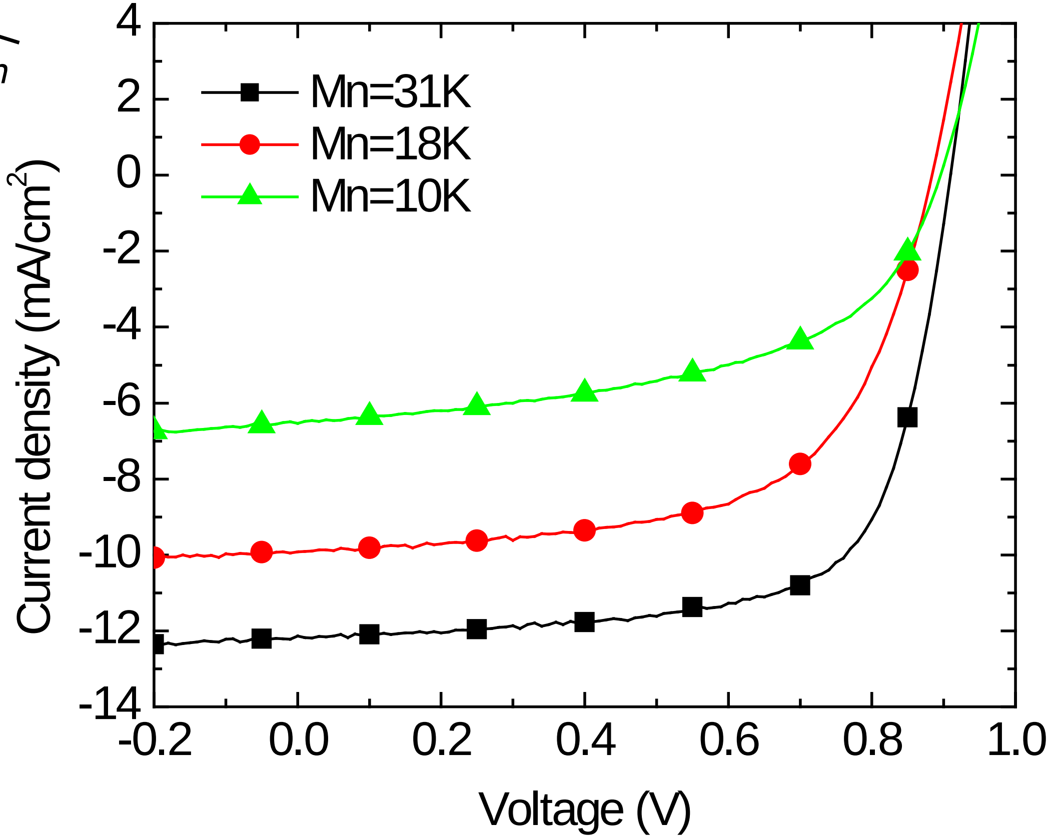


Published in: Ta-Ya Chu; Jianping Lu; Serge Beaupré; Yanguang Zhang; Jean-Rémi Pouliot; Salem Wakim; Jiayun Zhou; Mario Leclerc; Zhao Li; Jianfu Ding; Ye Tao; *J. Am. Chem. Soc.* **2011,** 133, 4250-4253.
DOI: 10.1021/ja200314m

Molecular Weight Effect

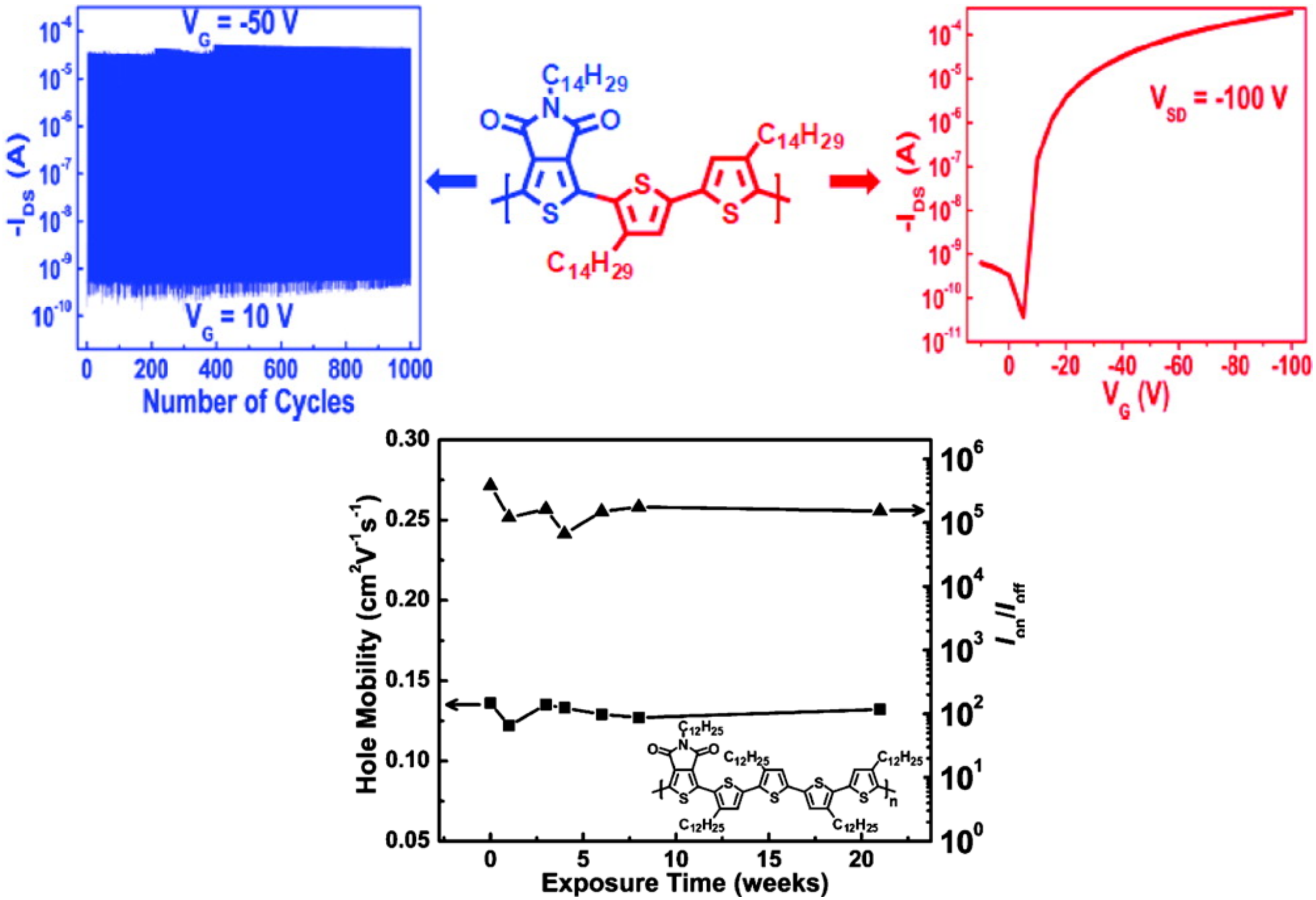


PCE: 7.5%
5.2%
3.0%



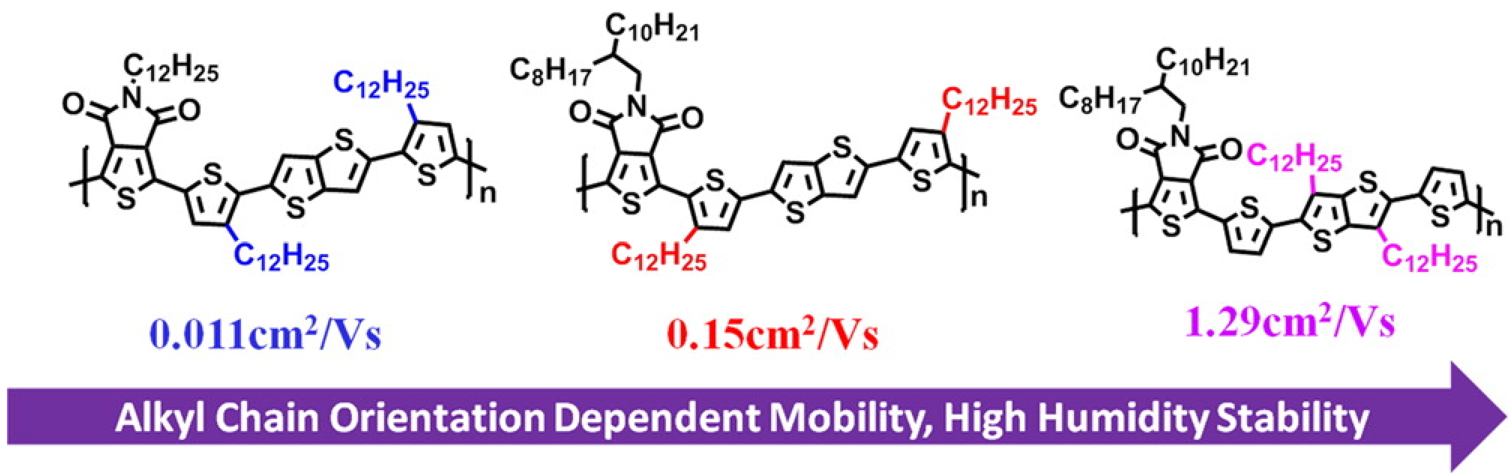
T.-Y. Chu, J. Lu, S. Beaupré, Y. Zhang, J.-R. Pouliot, J. Zhou, A. Najari, M. Leclerc, Y. Tao, *Adv. Funct. Mater.*, **2012,** 22, 2345.

OFETs



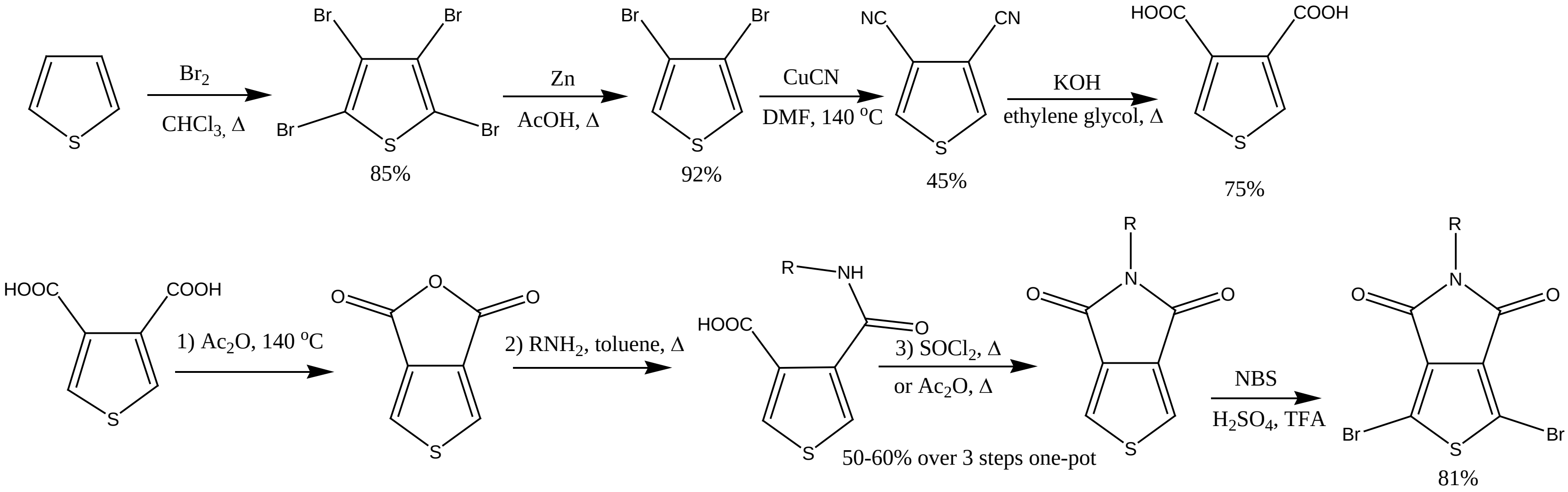
Published in: Xugang Guo; Rocio Ponce Ortiz; Yan Zheng; Myung-Gil Kim; Shiming Zhang; Yan Hu; Gang Lu; Antonio Facchetti; Tobin J. Marks; *J. Am. Chem. Soc.* **2011,** 133, 13685-13697.
DOI: 10.1021/ja205398u

OFETs

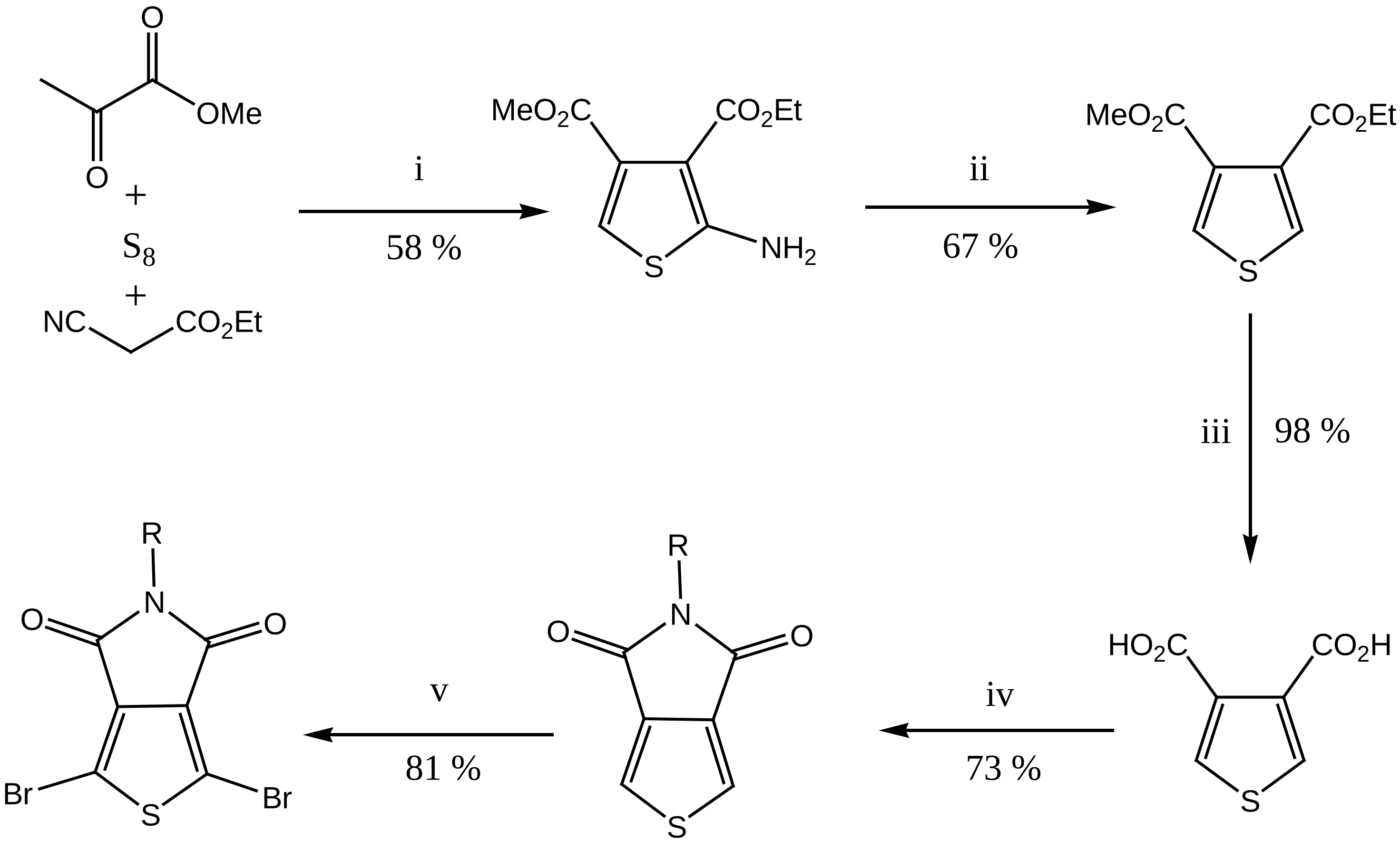


Published in: Qinghe Wu; Mao Wang; Xiaolan Qiao; Yu Xiong; Yangguang Huang; Xike Gao; Hongxiang Li; *Macromolecules* **2013,** 46, 3887-3894.
DOI: 10.1021/ma400544s

First Syntheses of TPD

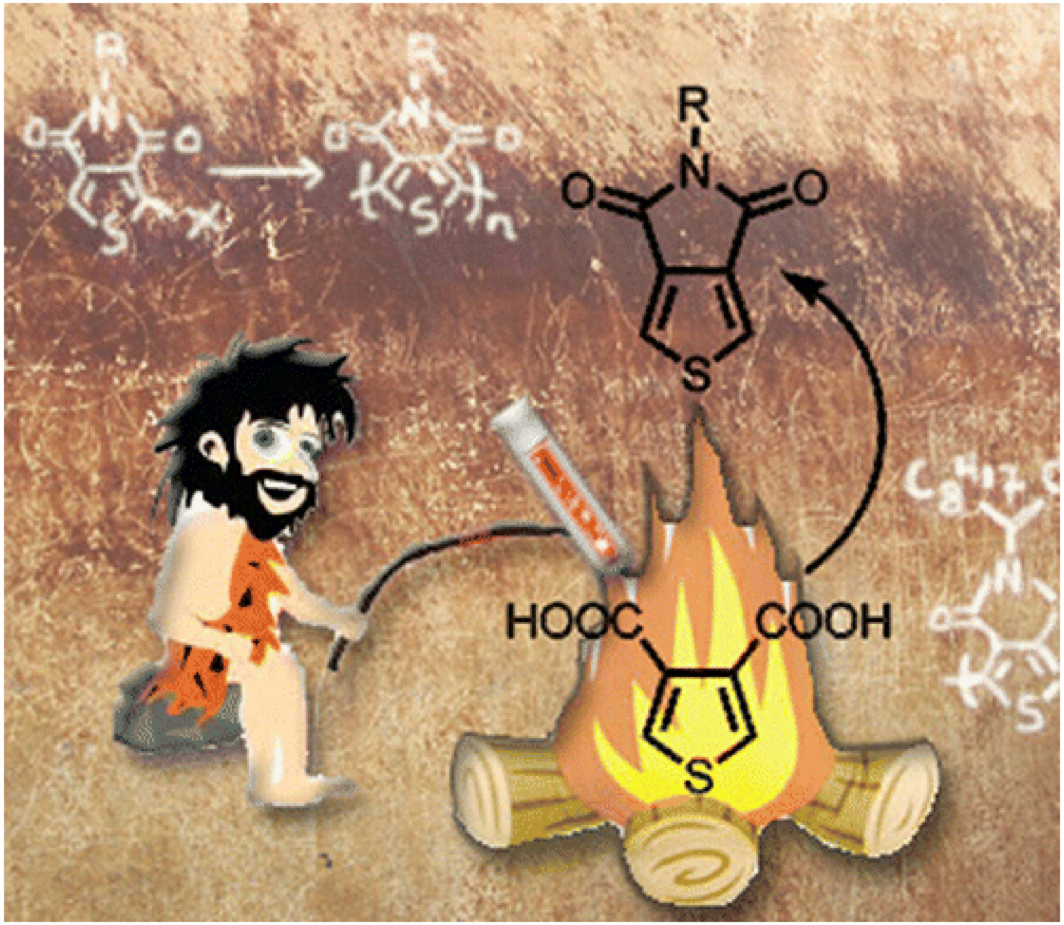


Synthesis of TPD Revisited

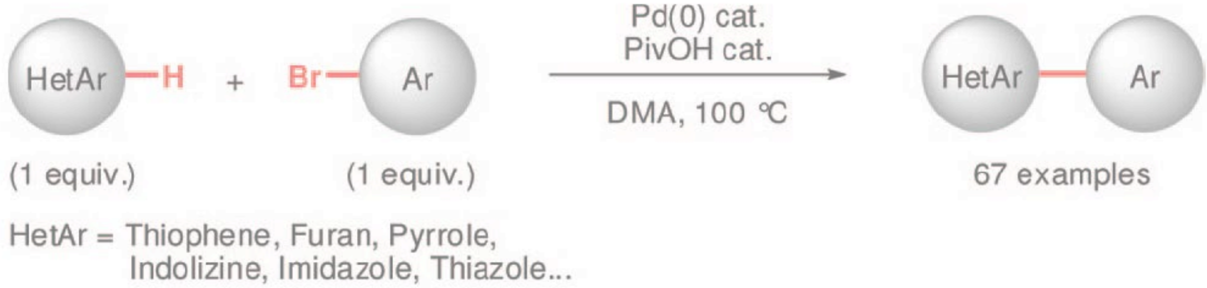


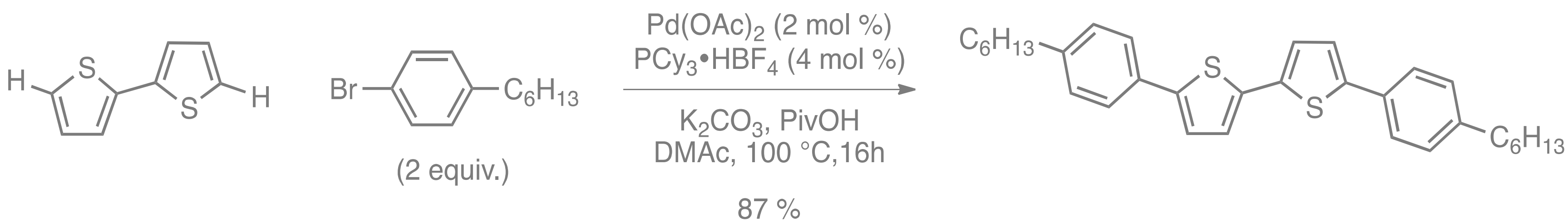
Conditions: i) Et_3N, DMF, 50 °C, 18h; ii) *t*-BuONO, THF, Δ, 3h; iii) 2M NaOH, Δ, overnight; iv) RNH_2, T ≥ 200 °C , 20 min; v) NBS, H_2SO_4, TFA, rt, overnight.

J. Org. Chem., 77, 8167 (2012).

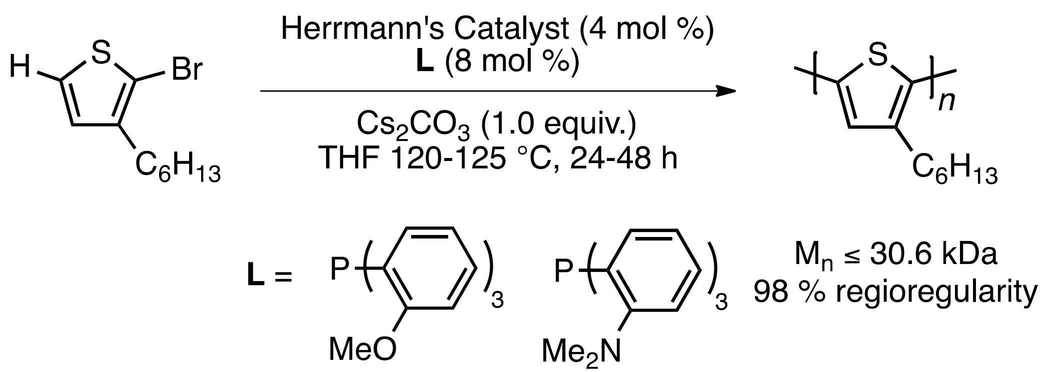

R
N
O
O
S
HOOC
COOH
S

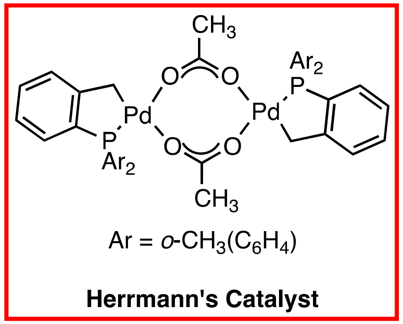
Direct (Hetero)Arylation



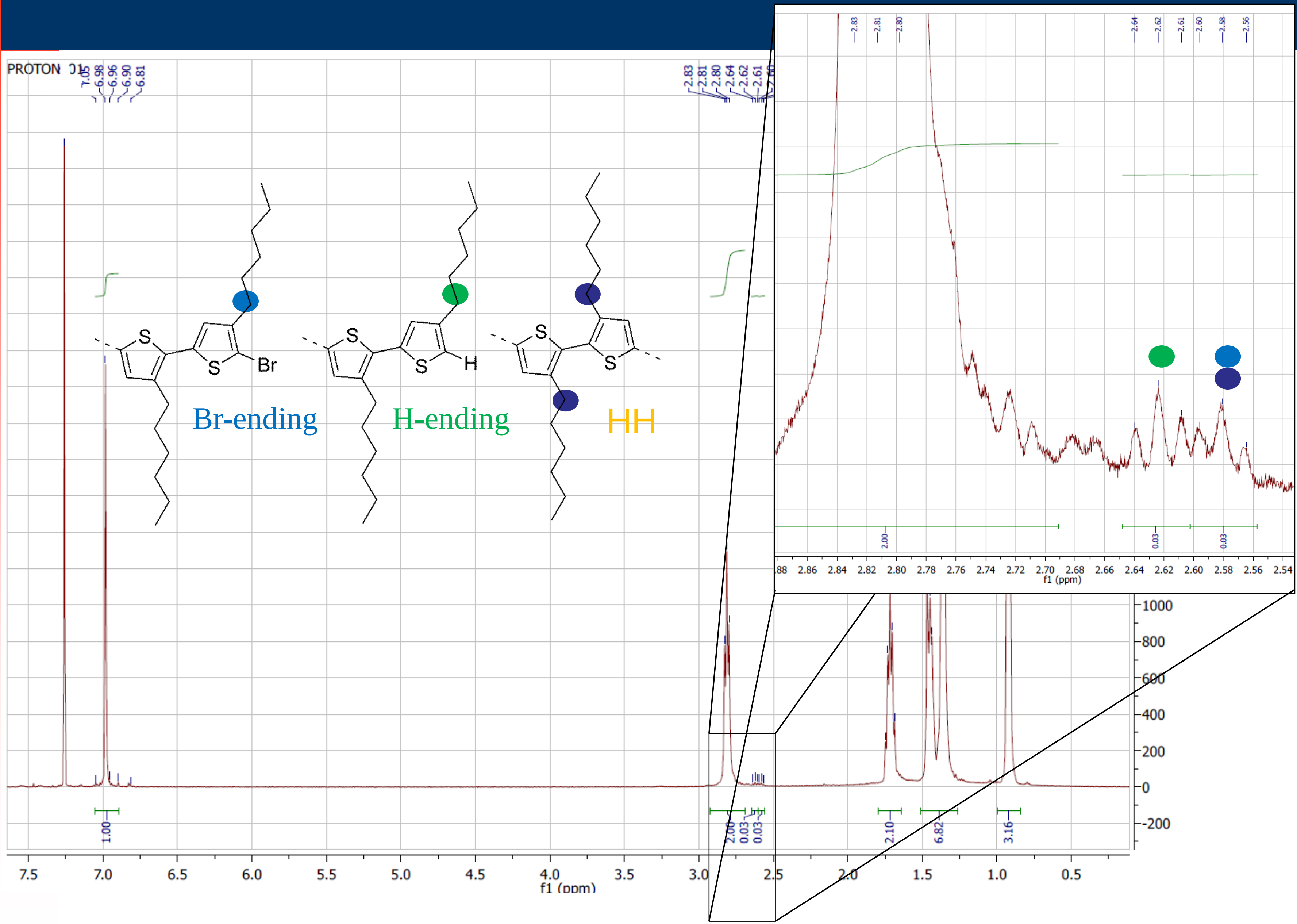


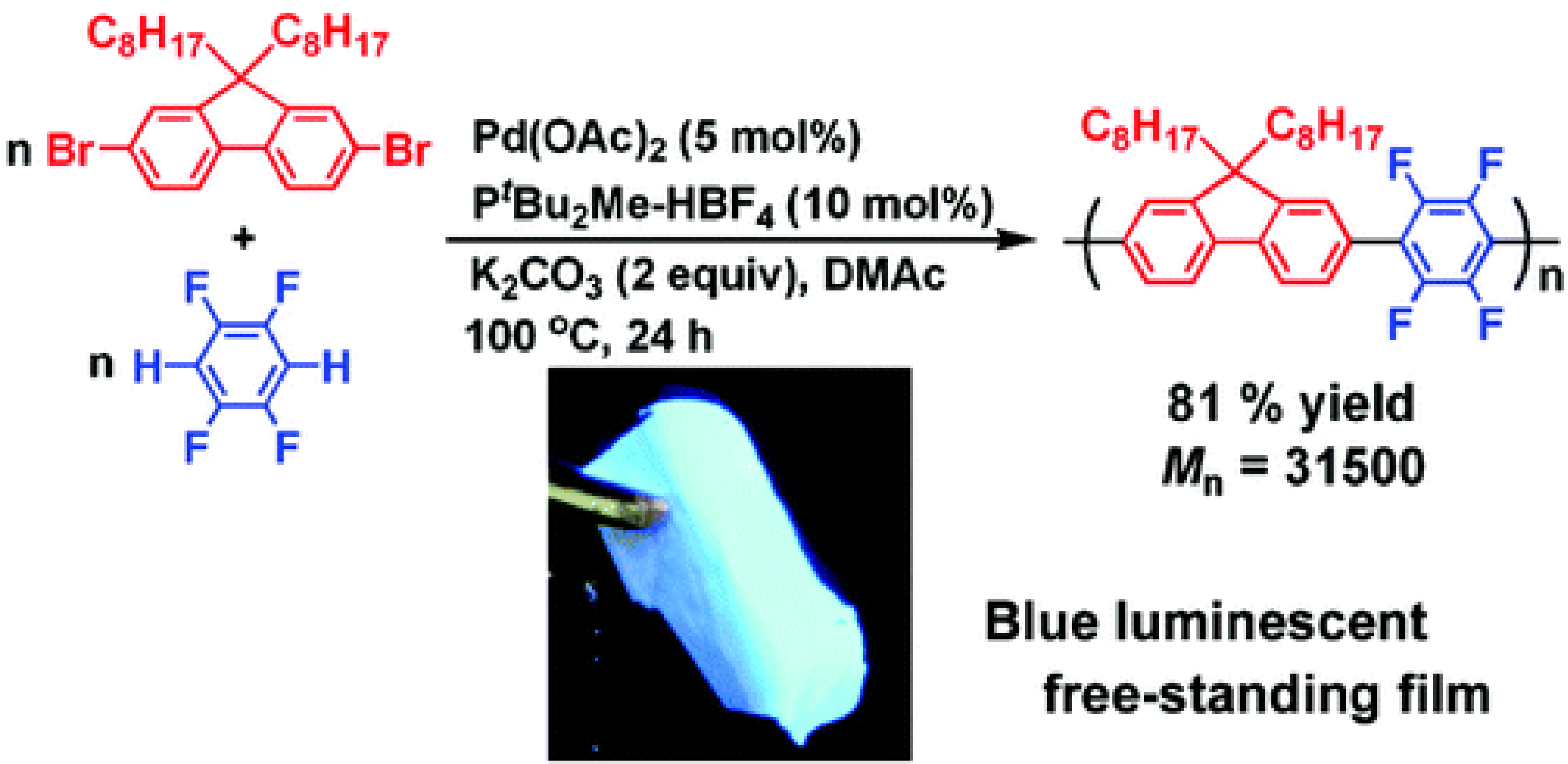
B. Liégault, D. Lapointe, L. Caron, A. Vlassova, K. Fagnou. *J. Org. Chem.* **2009,** *74,* 1826.
D. J. Schipper, K. Fagnou. *Chem. Mater.* **2011**, *23,* 1594.





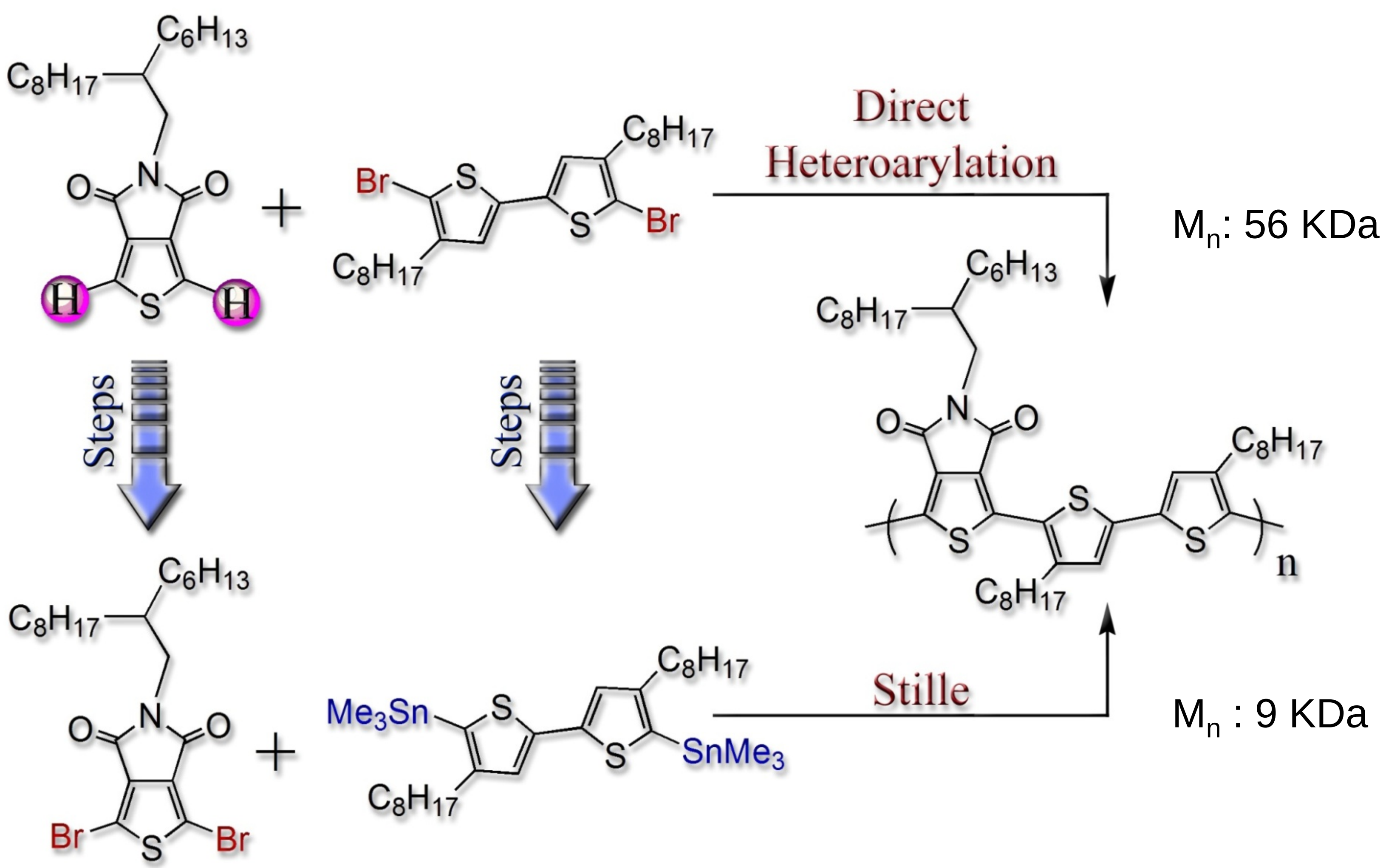
Q. Wang, R. Takita, Y. Kikuzaki, F. Ozawa. *J. Am. Chem. Soc.* **2010,** *132,* 11420.


PROTON_01
Br-ending
H-ending
HH
Br
H
S
f1 (ppm)



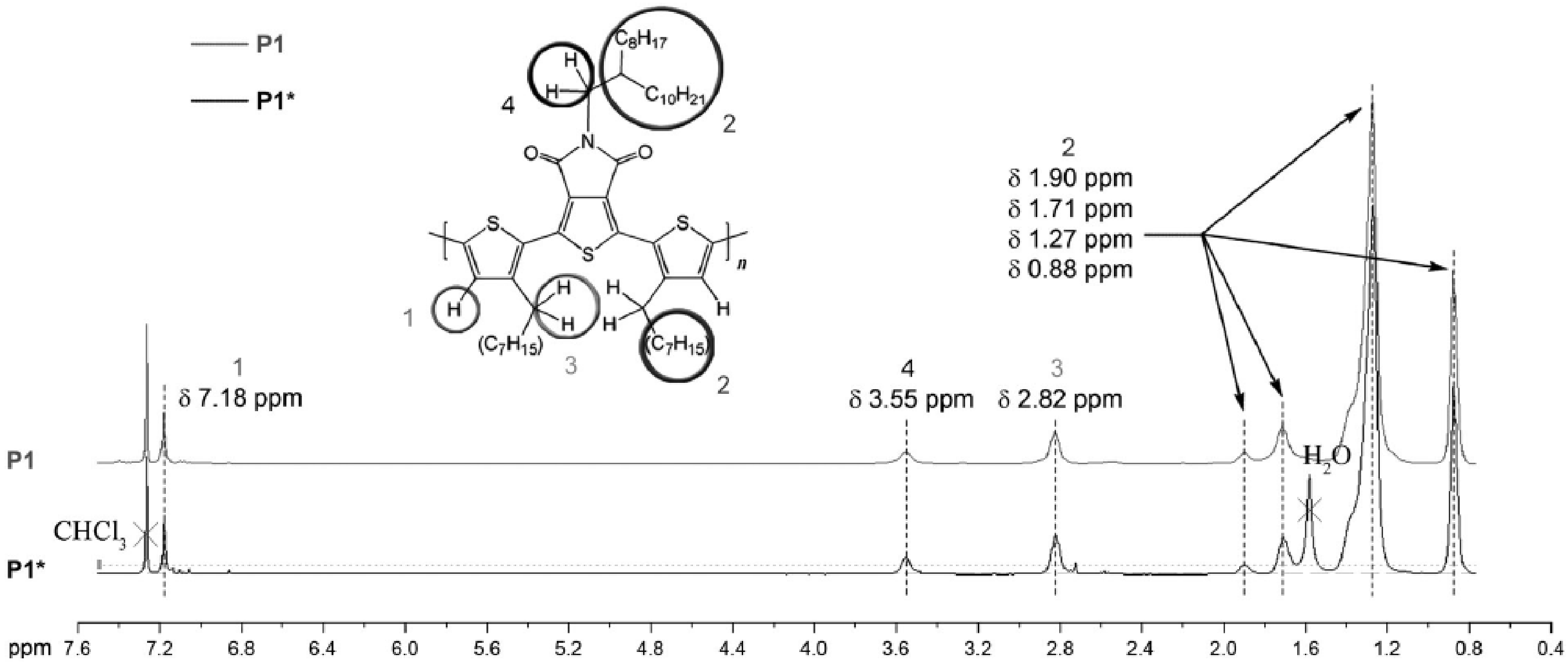
W. Lu, J. Kuwabara, T. Kanbara, Macromolecules 44, 1252 (2011)

Direct Heteroarylation

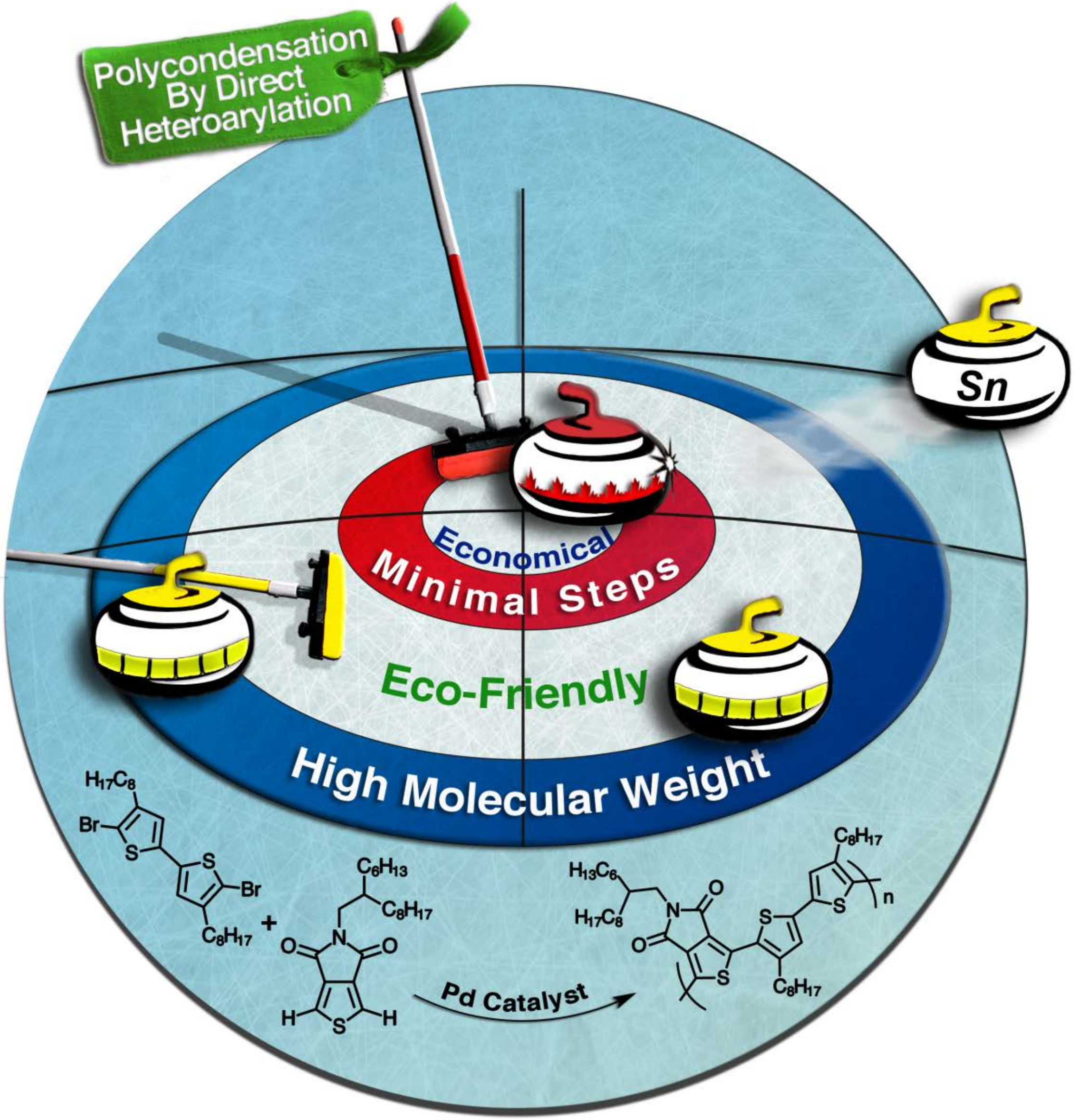


Angew. Chem. Int. Ed., VIP paper, 51, 2068, (2012)

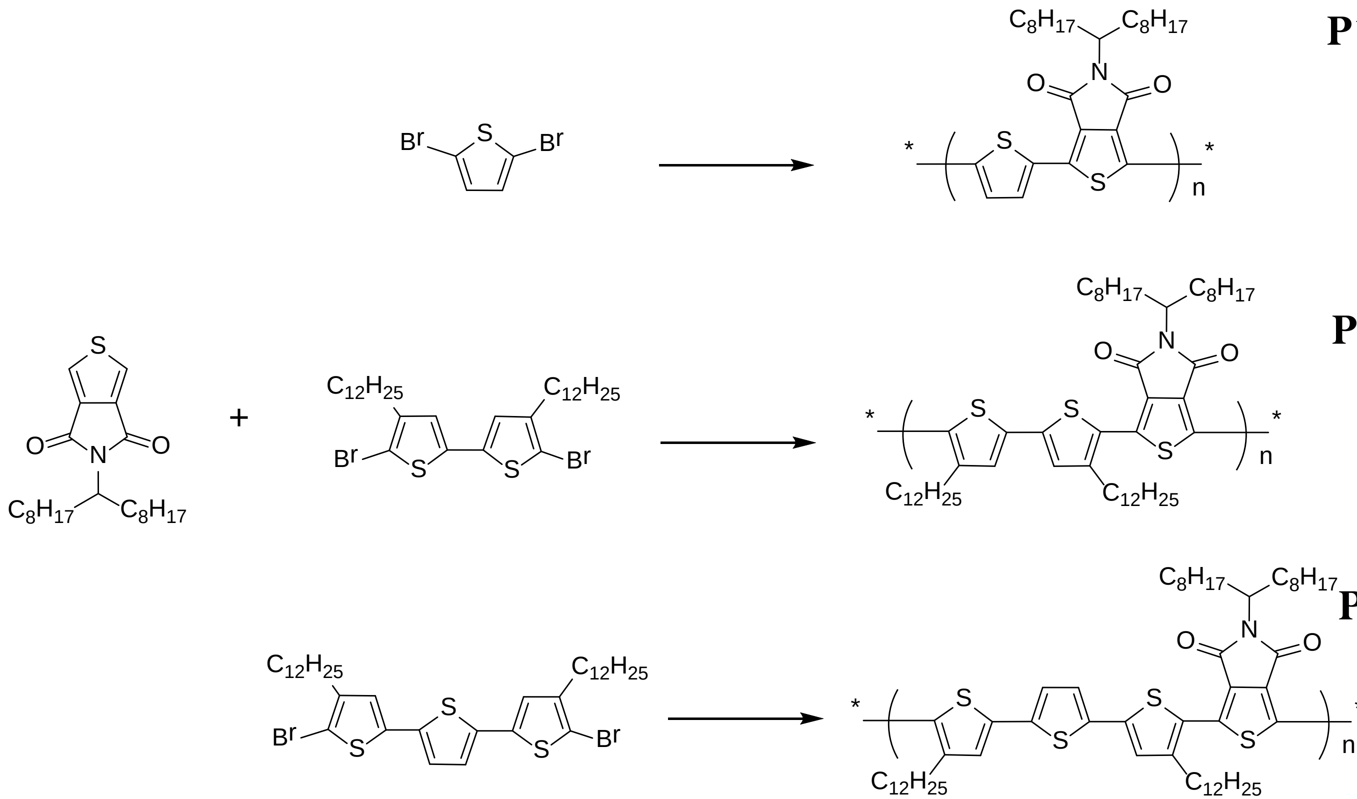
^{1}H NMR Analyses



Direct (Hetero)arylation Polycondensation



Synthesis of TPD-based Copolymers via Direct Heteroarylation



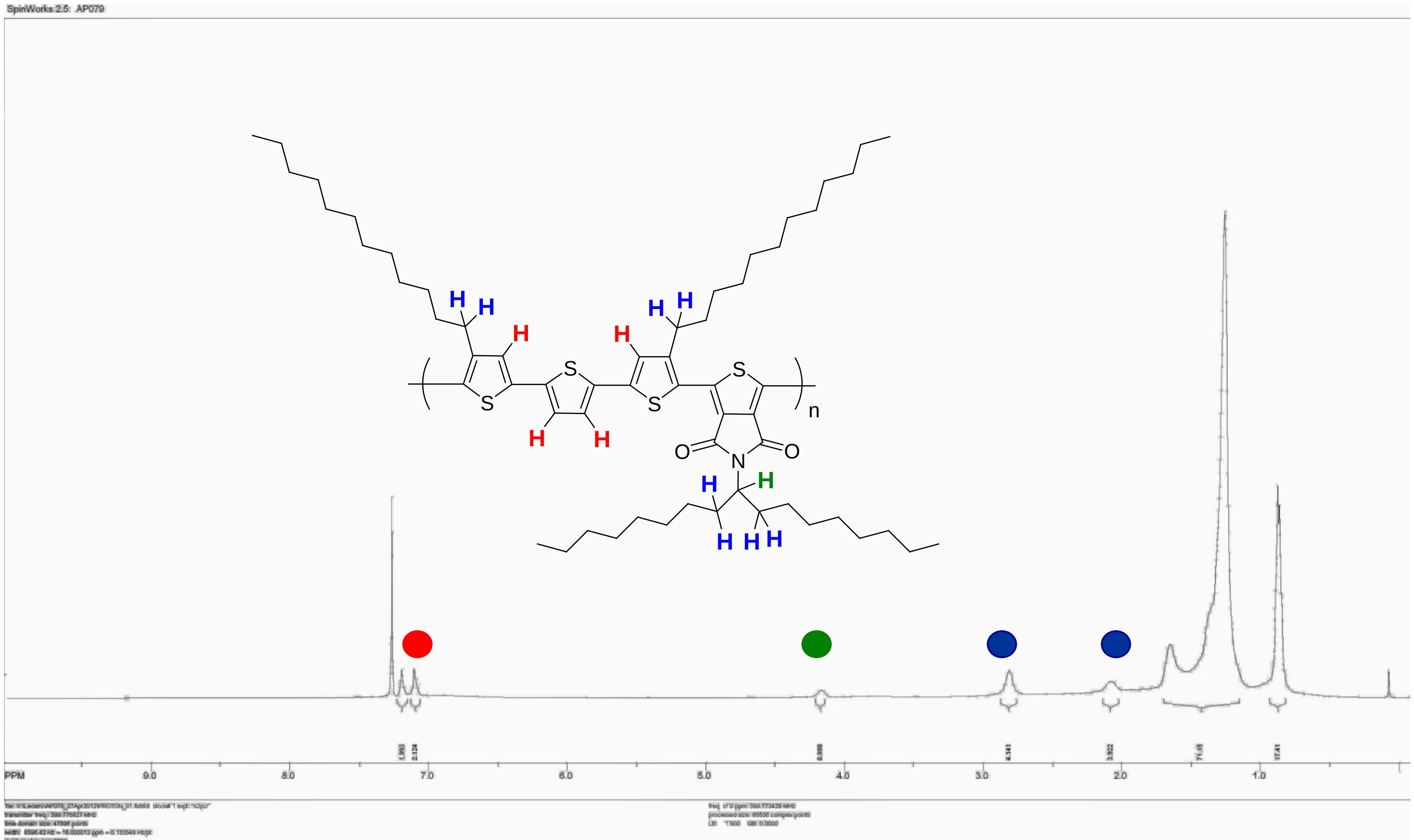
P1 Mn = 16 kDa
PDI = 2.6
Yield = 62%

P2 Mn = 50 kDa
PDI = 2.0
Yield = 94%

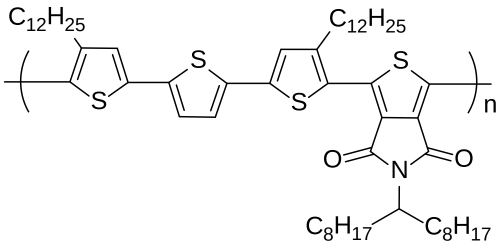
P3 Mn = 48 kDa
PDI = 2.5
Yield 92%

Polymerization conditions: Herrmann-Beller catalyst, (o-anisyl)$_3$P, Cs_2CO_3, PivOH, toluene, 120^{o}C, 17-24 h

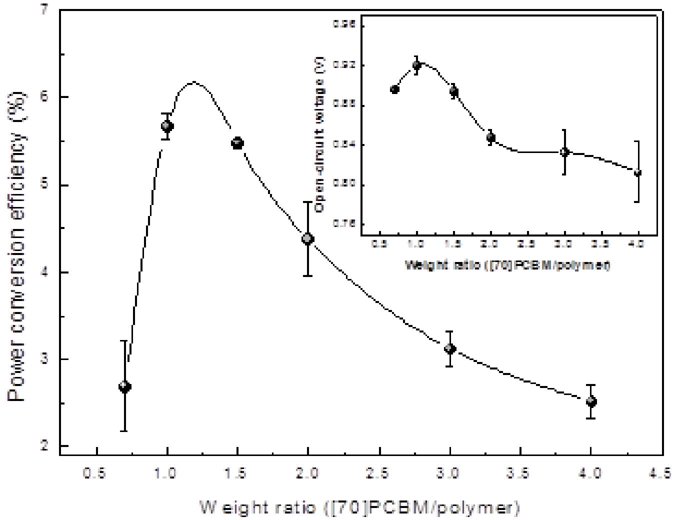
^1H NMR of **P3**



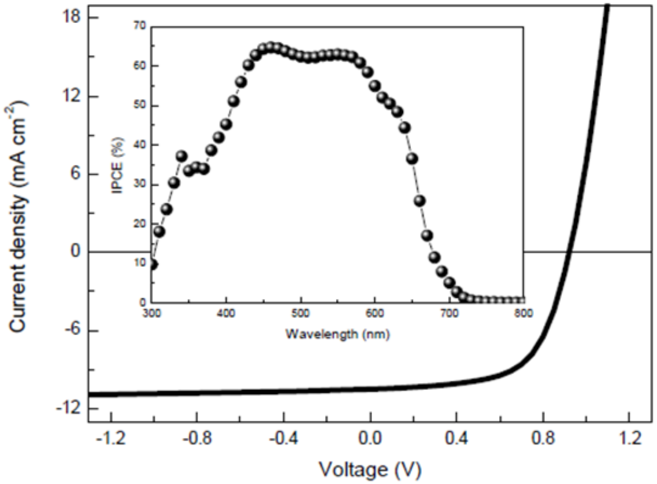
OPV Devices - Best results



P3

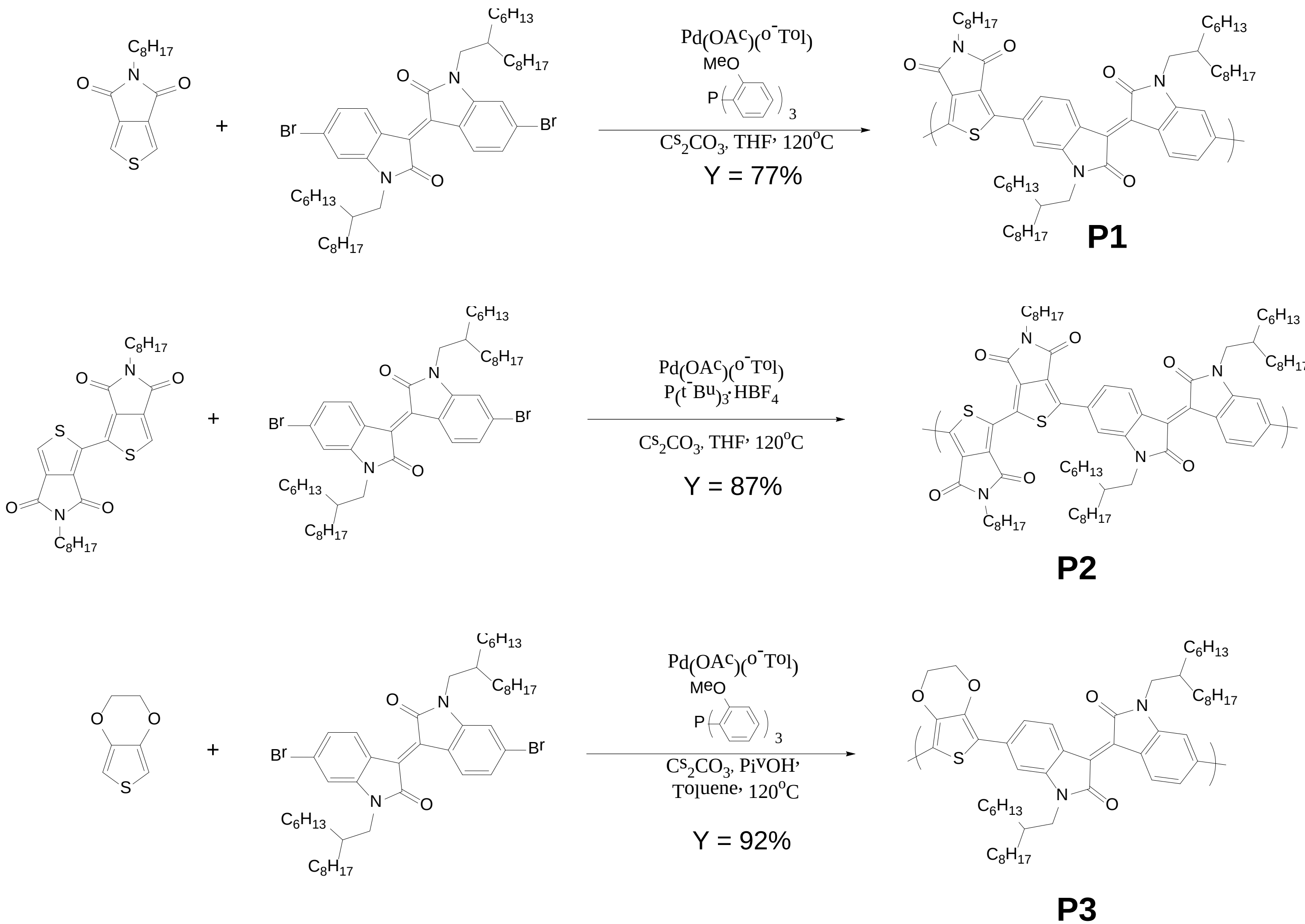


Voc = 0.92 V
Jsc = -10.51 mA/cm2
FF = 0.63
PCE = 6.1%



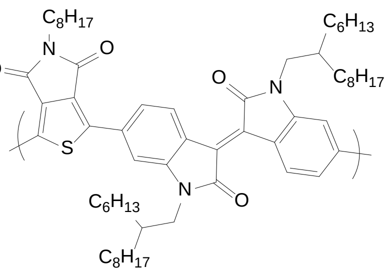
J. Jo, A. Pron, P. Berrouard, W. L. Leong, J. D. Yuen, J. S. Moon, M. Leclerc, A. J. Heeger *Adv. Energy Mater.*, 2, 1397 (2012).

Isoindigo polymers

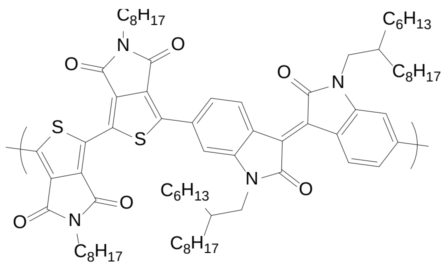


Polym. Chem., **2013**, *4*, 1836-1841

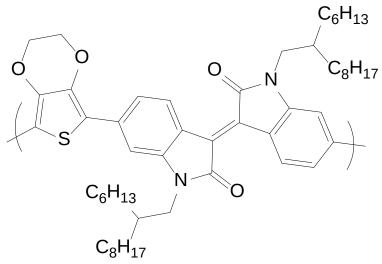
Isoindigo polymers



P1



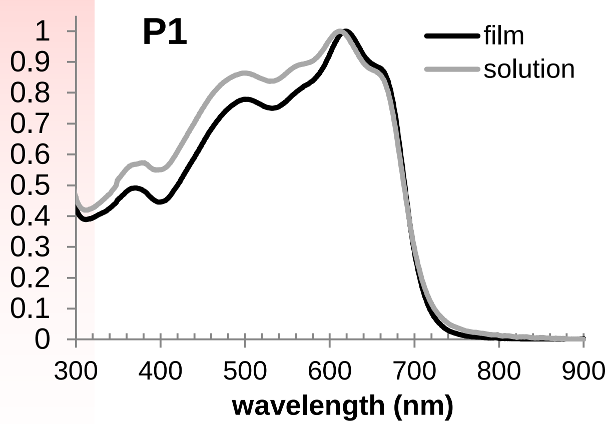
P2

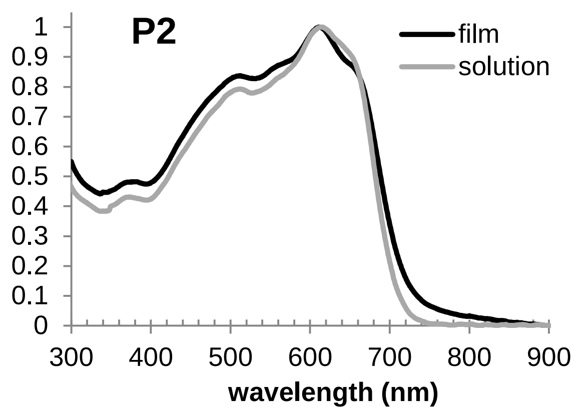


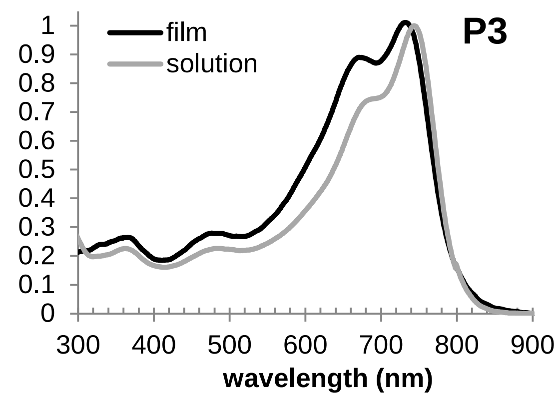
P3

Table 1: Properties of the isoindigo copolymers **P1**, **P2** and **P3**

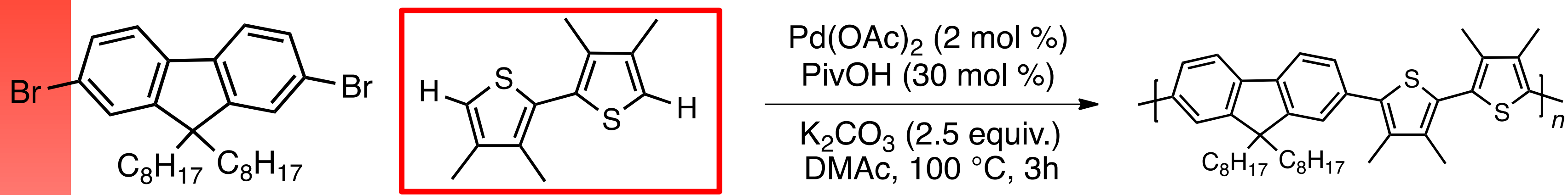
Polymer	Mn	Mw	HOMO	LUMO	Eg^{elec}	Eg^{opt}
	kg/mol	kg/mol	eV	eV	eV	eV
P1	24	53	-6.0	-4.2	1.8	1.72
P2	20	43	-6.1	-4.2	1.9	1.75
P3	85	200	-5.4	-3.9	1.5	1.55



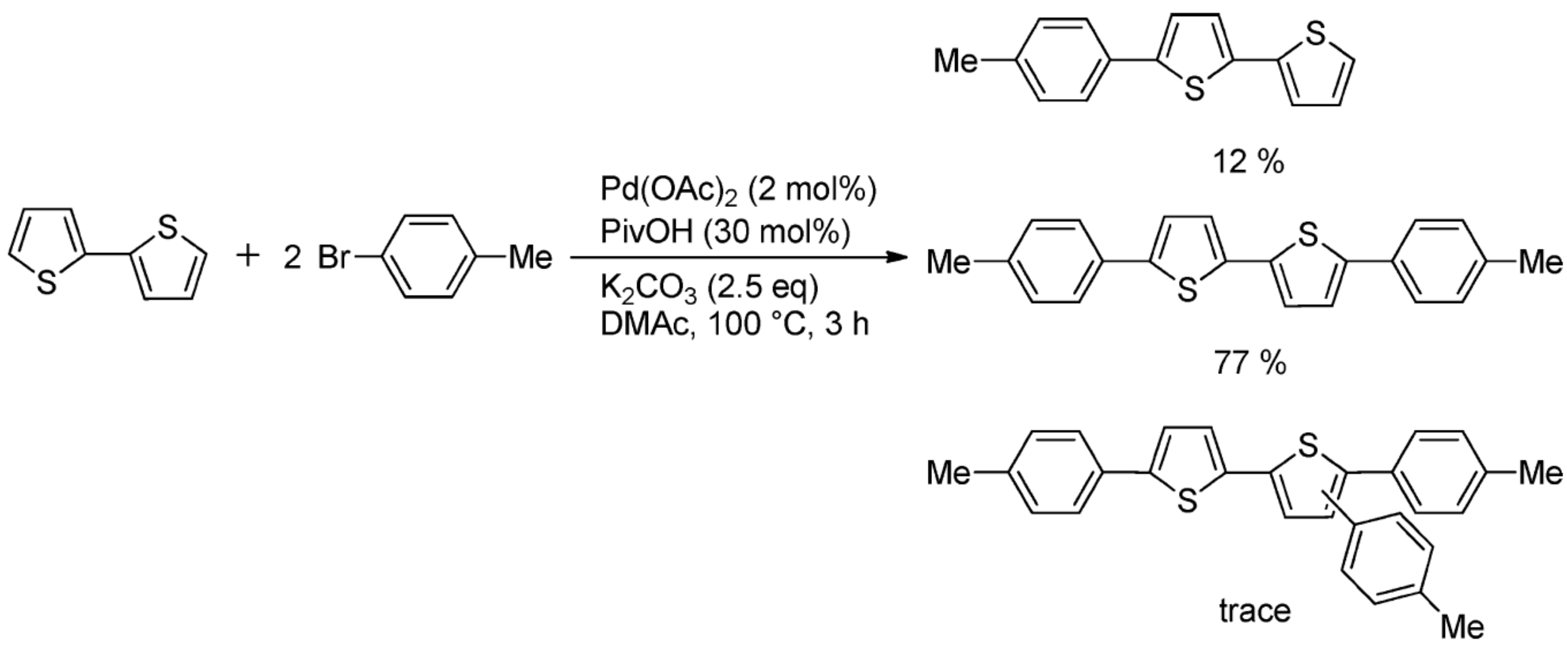




Cross-Linking

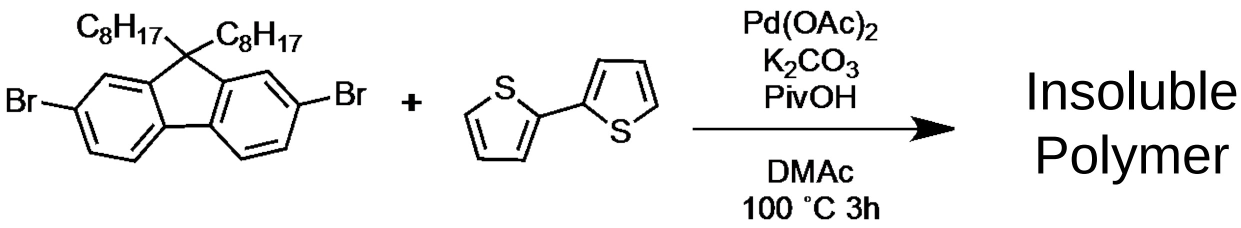


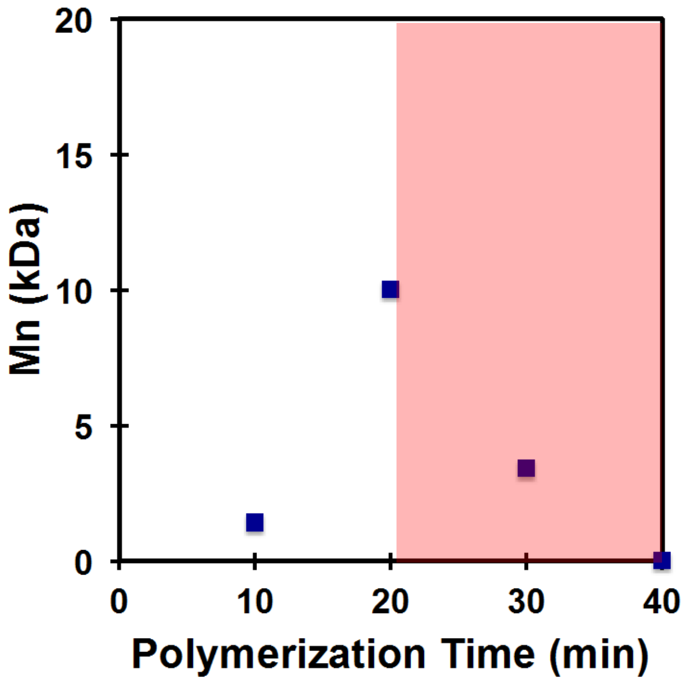
M_n = 32 kDa, PDI = 2.5



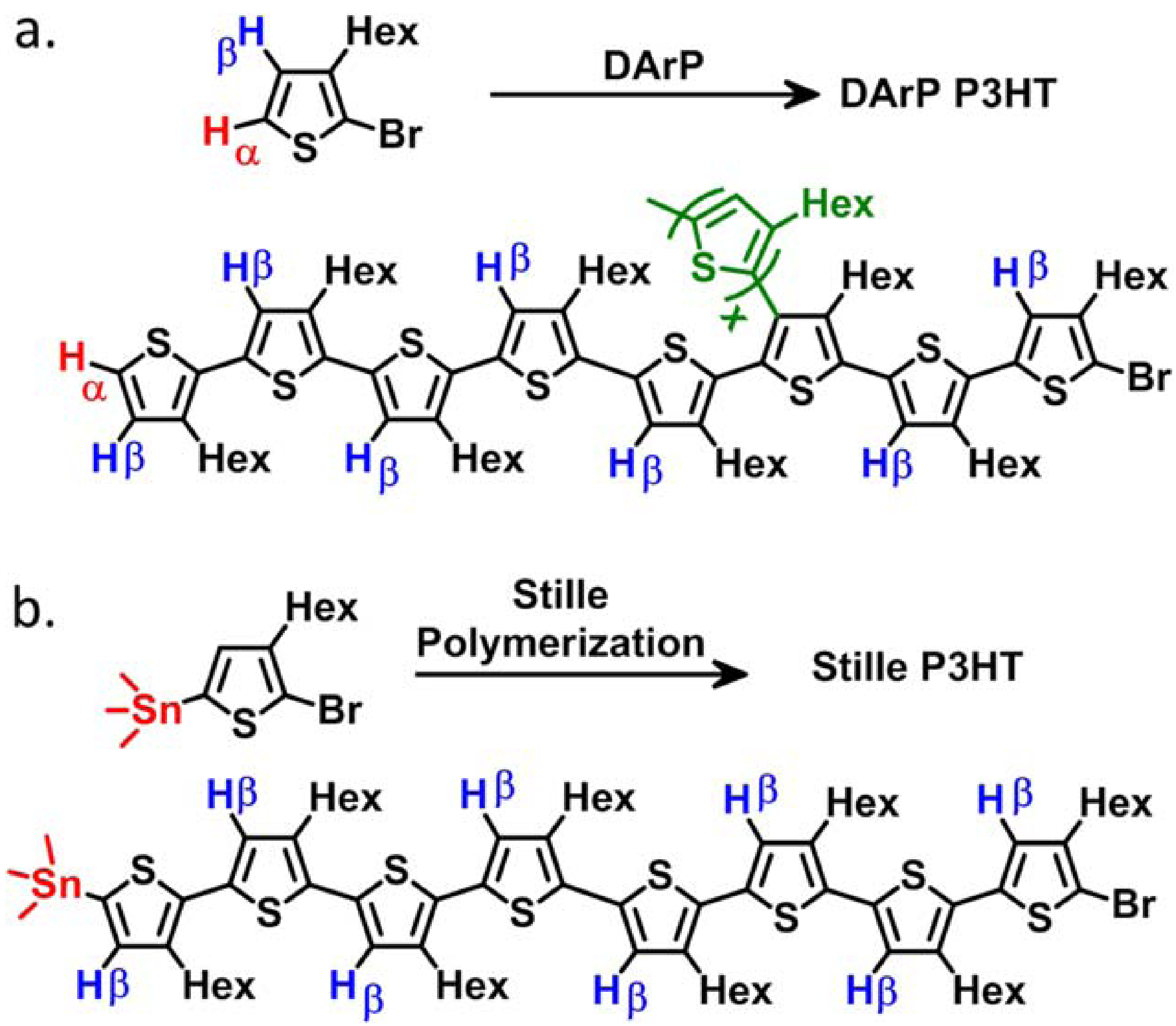
Y. Fujinami, J. Kuwabara, W. Lu, H. Hayashi, T. Kanbara. *ACS Macro Lett.* **2012,** *1,* 67.

Kinetics

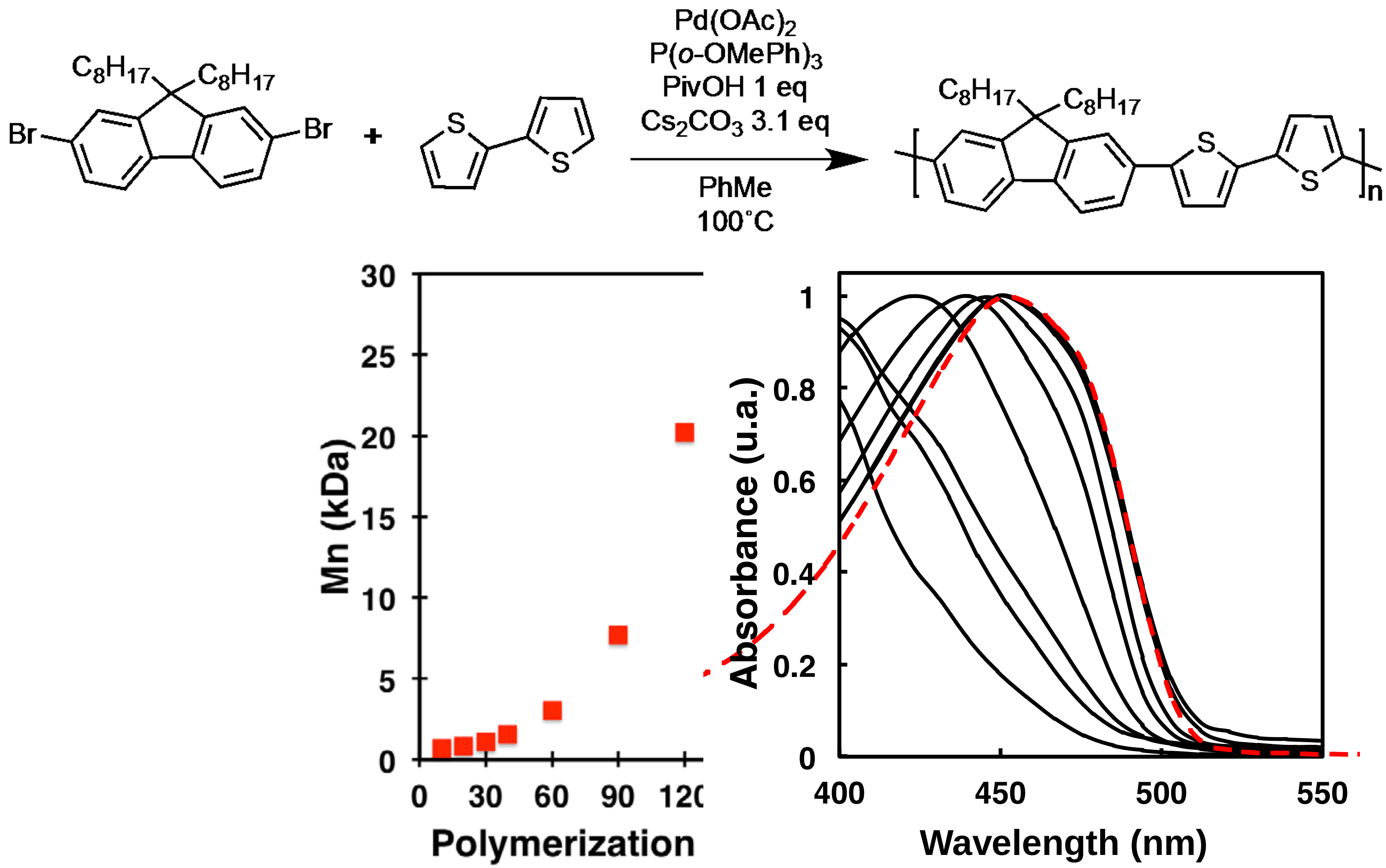




Y. Fujinami, J. Kuwabara, W. Lu, H. Hayashi, T. Kanbara. *ACS Macro Lett.* **2012,** *1,* 67.

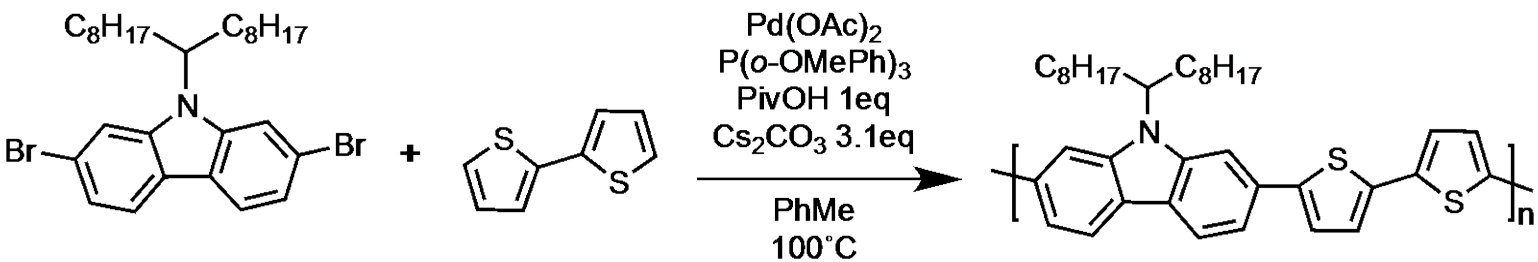

a.
DArP
DArP P3HT
b.
Stille
Polymerization
Stille P3HT

Kinetics

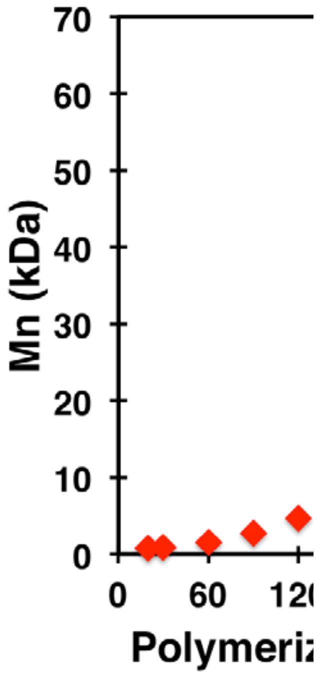


C8H17
C8H17
Br
Br
+
S
S
Pd(OAc)2
P(o-OMePh)3
PivOH 1 eq
Cs2CO3 3.1 eq
PhMe
100˚C
n
Mn (kDa)
Polymerization
Absorbance (u.a.)
Wavelength (nm)

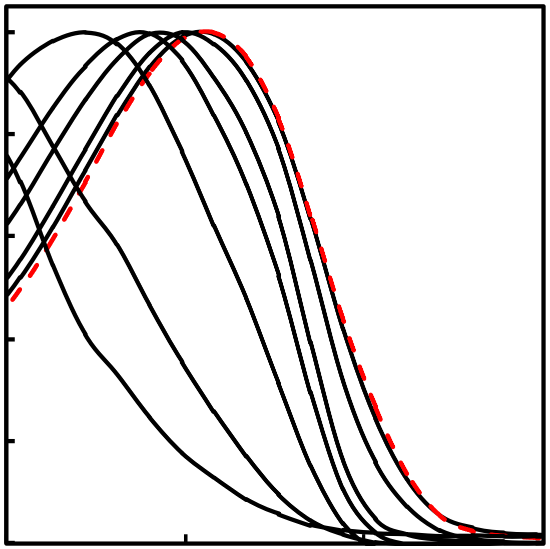
Kinetics



C8H17
C8H17
N
Br
Br
+
S
S
Pd(OAc)2
P(o-OMePh)3
PivOH 1eq
Cs2CO3 3.1eq
PhMe
100˚C
n

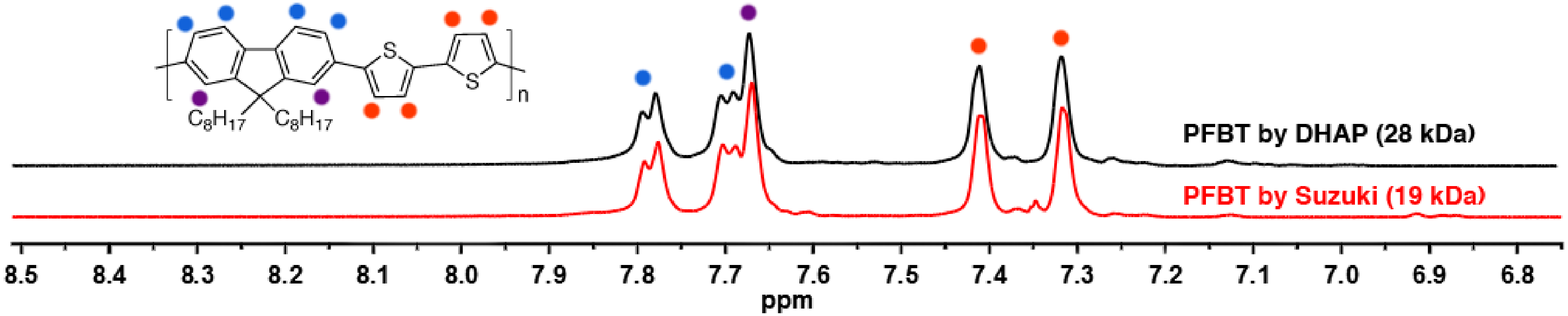


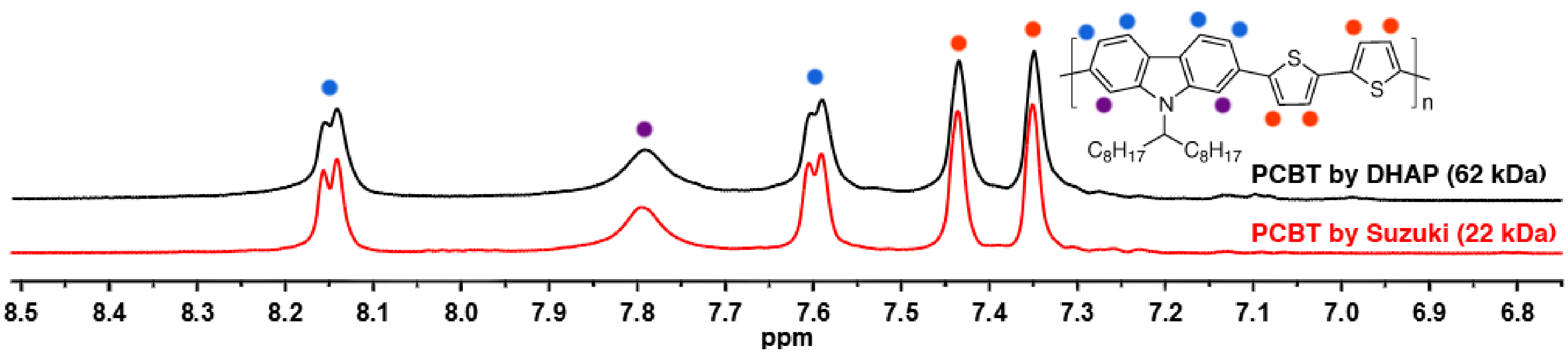
70
60
50
40
30
20
10
0
Mn (kDa)
0
60
Polymeri



Wavelength (nm)

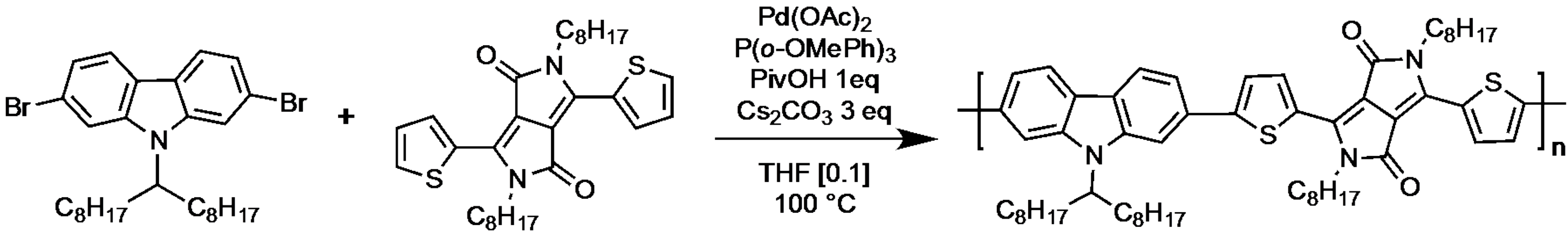
^{1}H NMR

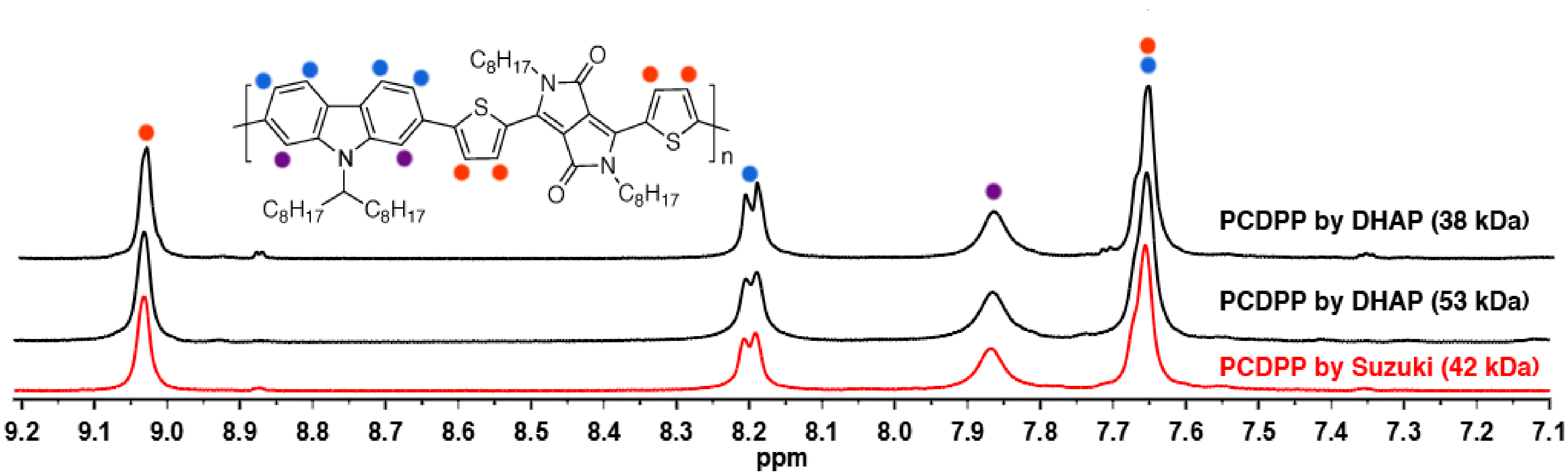




TCE, 500MHz, 90 ˚C

Cbz-DPP





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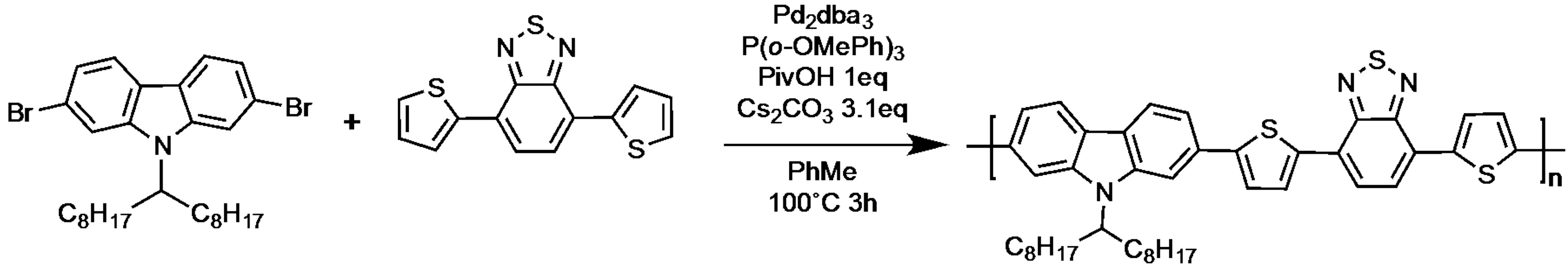
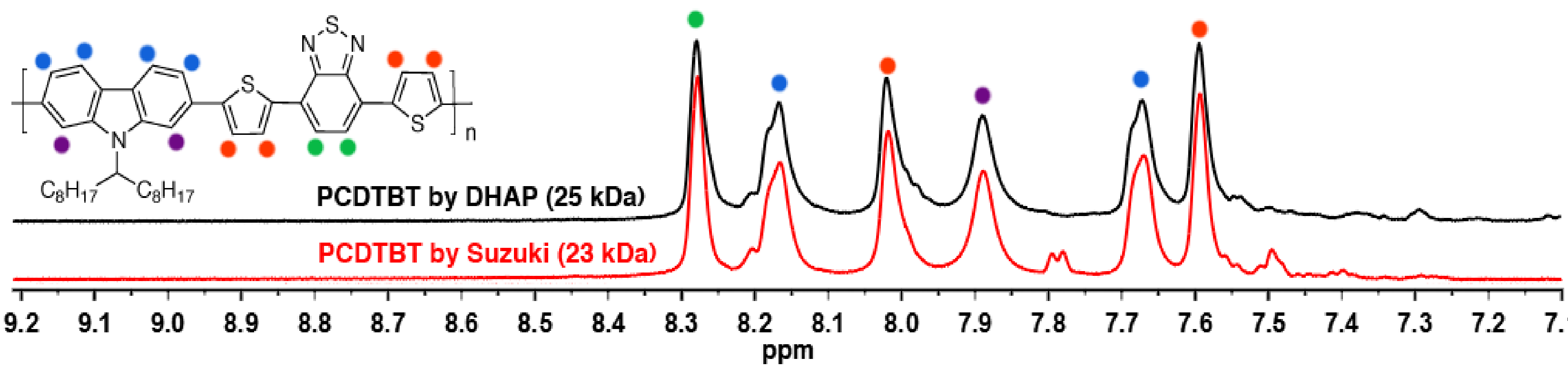
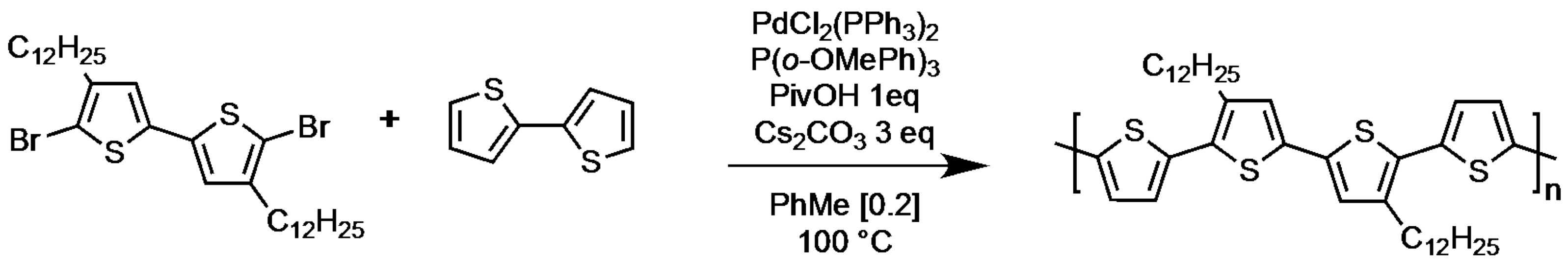
PCDTBT

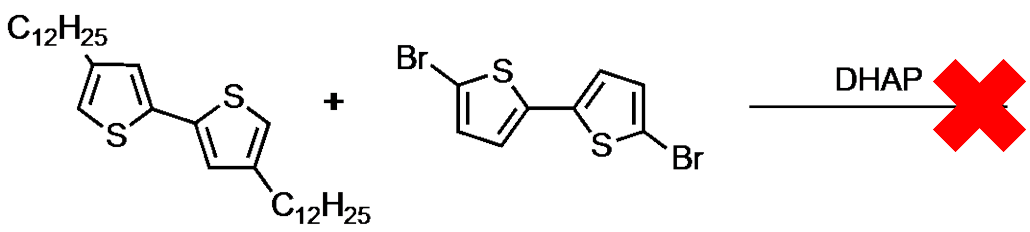




TCE, 500MHz, 90 ˚C

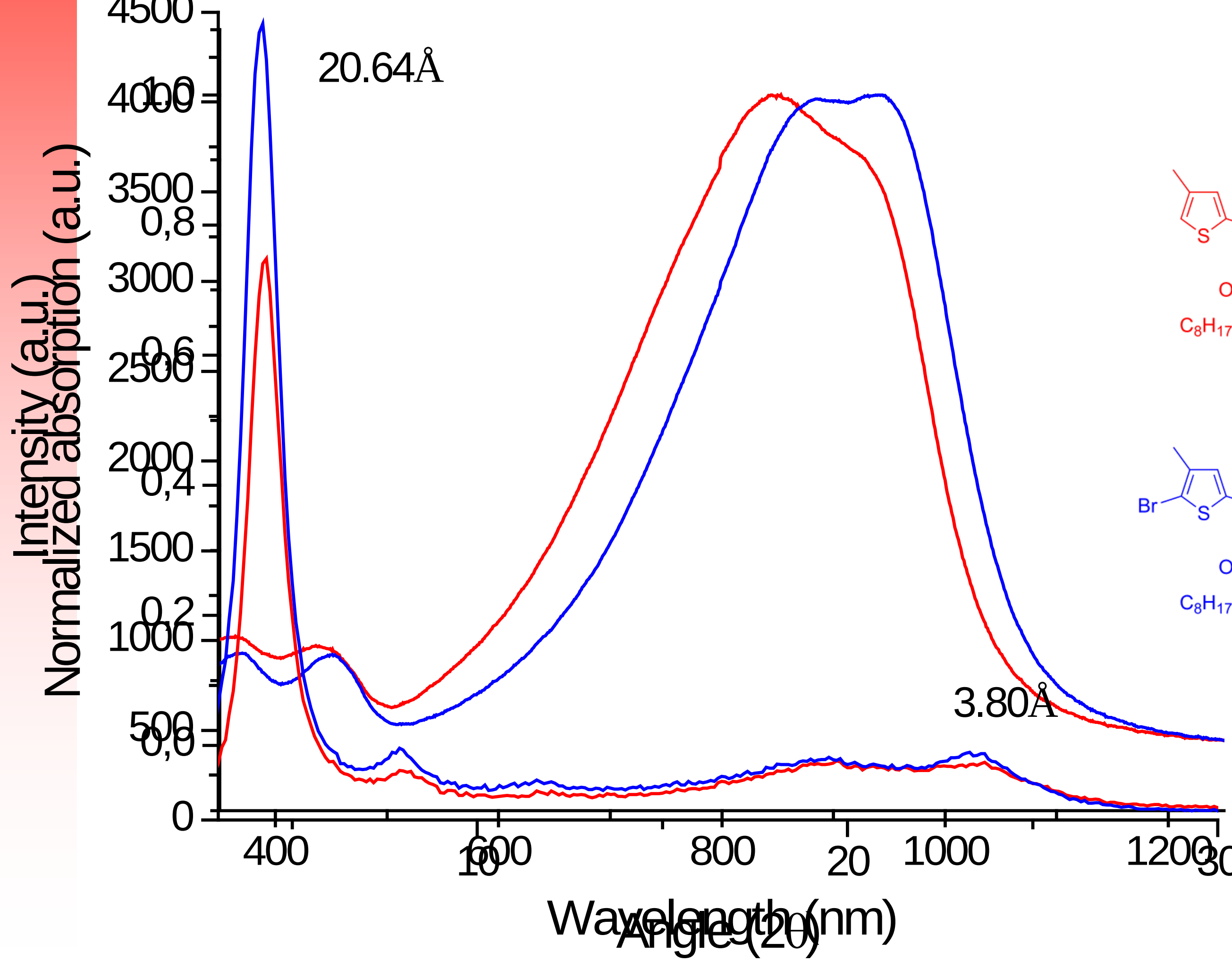
Bithiophene-bithiophene



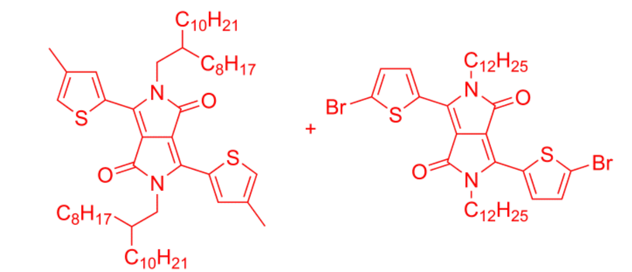


DHAP - DPP

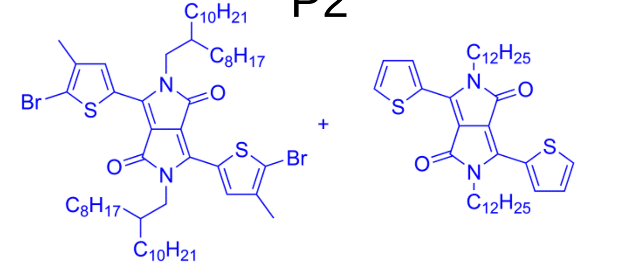
Polymer	M_n kDa	M_p kDa	$Đ_m$	E_g^{Opt} eV	LUMO eV	HOMO eV	E_g^{CV} eV	μ_h $cm^2/V \cdot s$	$I_{on/off}$	V_{thres} V
P1	15	51	3.4	1.13	-4.08	-5.35	1.27	0.26	10^5	-2
P2	46	114	2.5	1.12	-4.06	-5.29	1.23	**1.17**	10^3	0



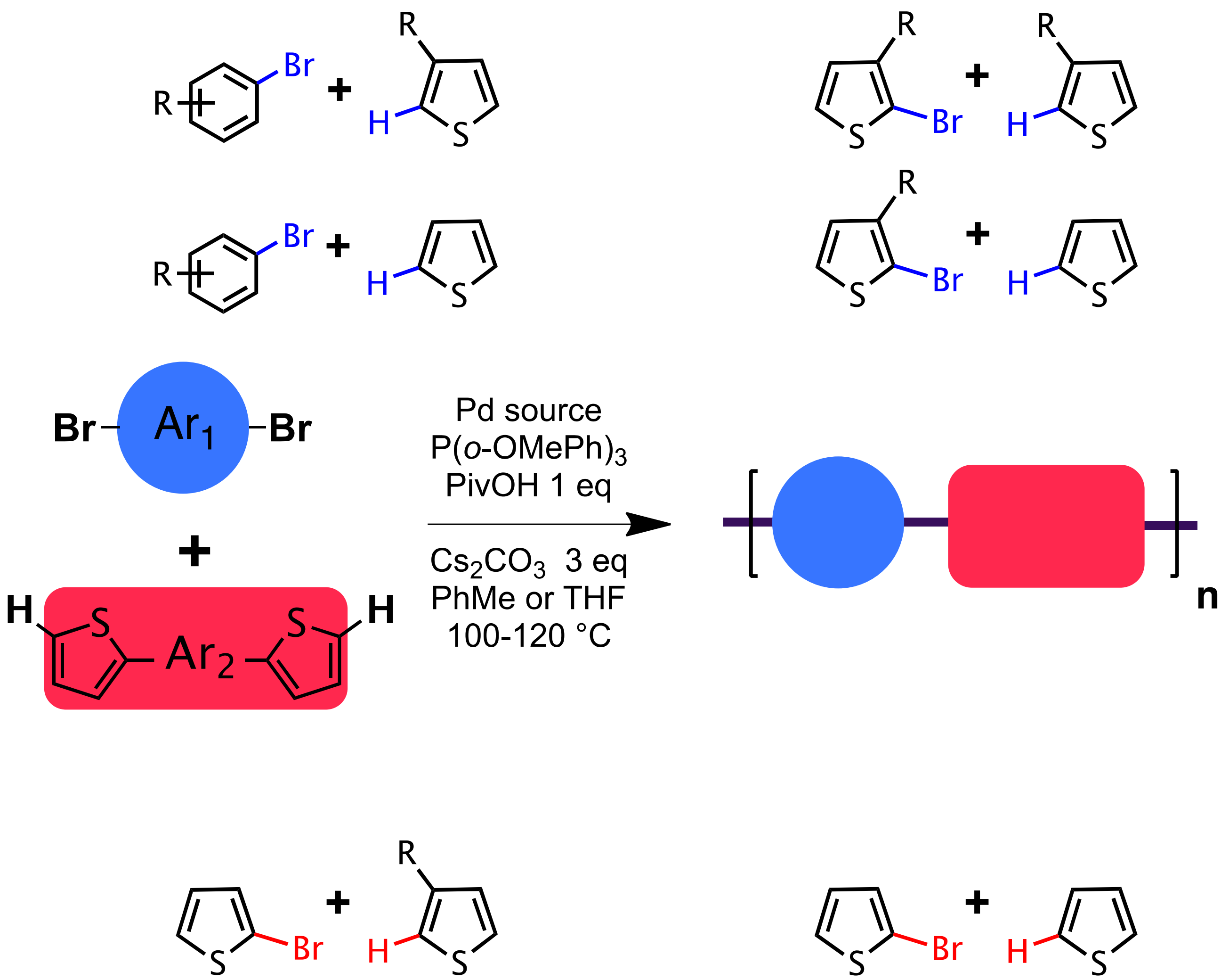
P1



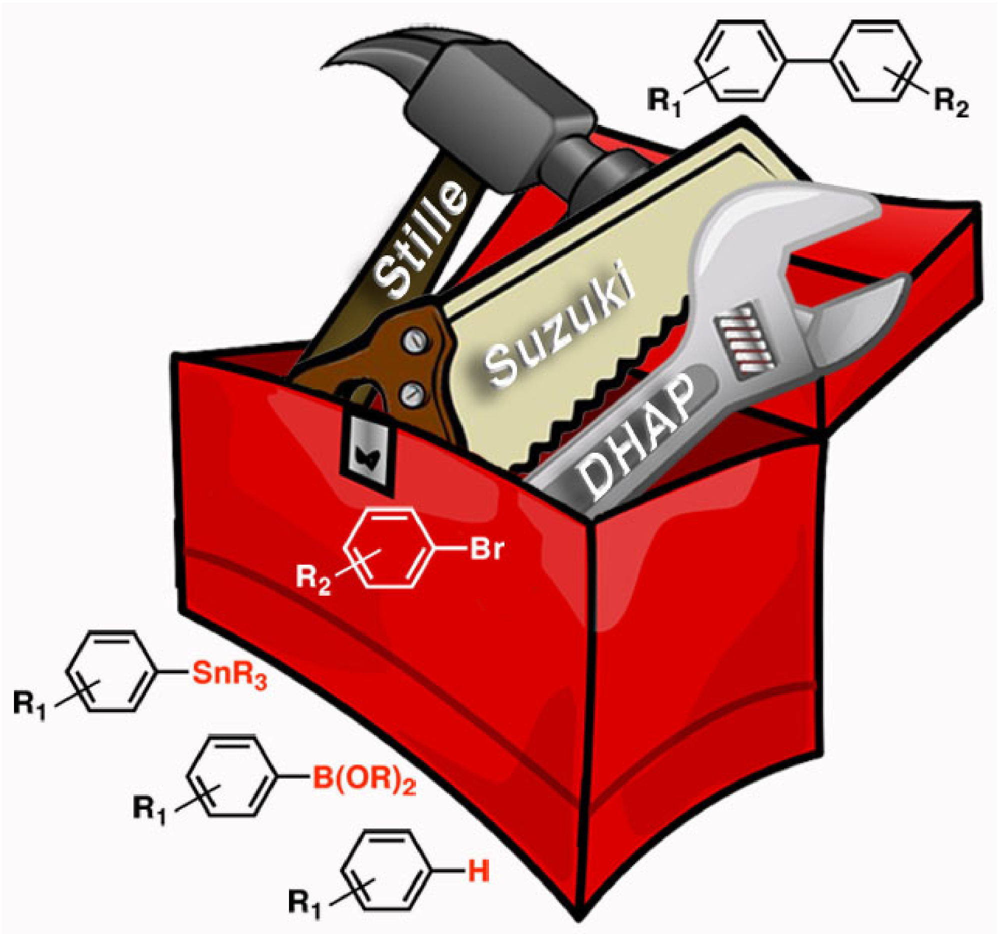
P2



Conclusions



Direct (Hetero)arylation Polycondensation

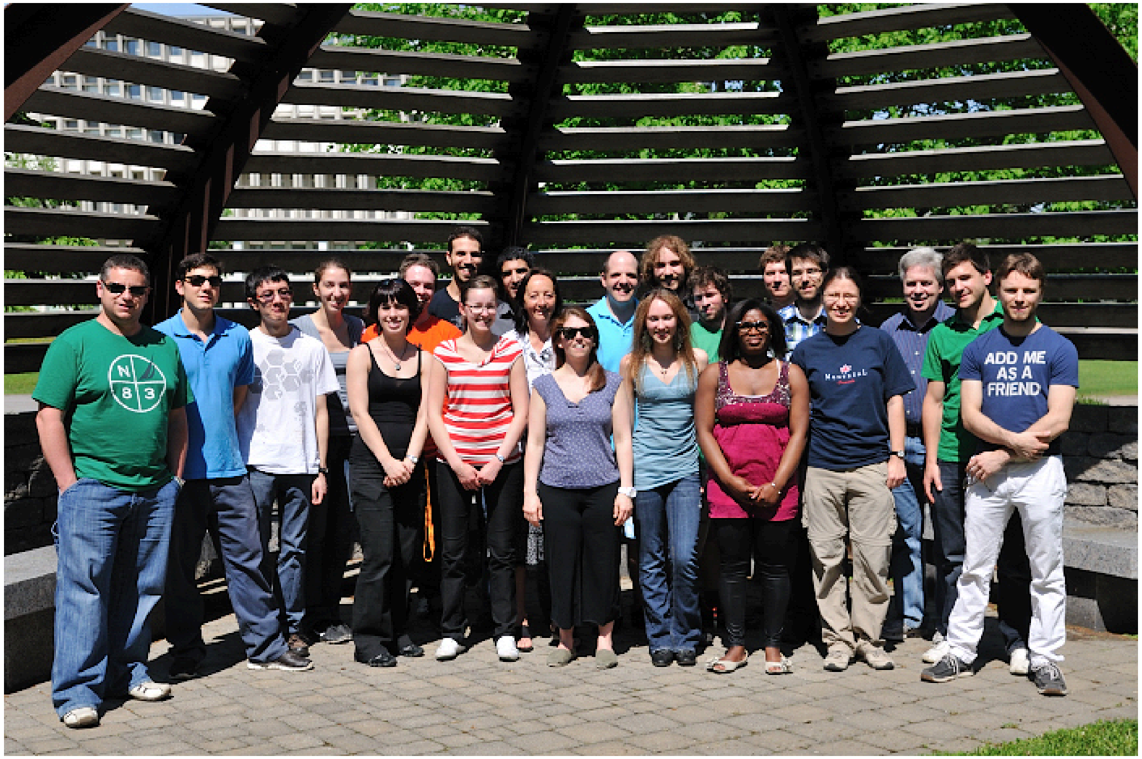


L.G. Mercier., M. Leclerc, Acc. Chem. Res. **2013**, 46, 1597-1605

$$$

- CANADA RESEARCH CHAIR PROGRAM
- NSERC (DISCOVERY, STRATEGIC, NETWORK)
- CANADIAN FOUNDATION for INNOVATION
- STDC PROGRAM
- MDEIE (PSVT Program)
- FRQNT (CQMF, Actions Concertées)
- US ARMY
- NANOQUÉBEC (NanoULaval)
- HYDRO-QUEBEC + NSERC (CRD)

Acknowledgment



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